FURTHER INVESTIGATION OF FLUOBORIC ACID IN SANDSTONE ACIDIZING USING ^{11}B AND ^{19}F NMR

A Thesis

by

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ABSTRACT

Although fluoboric acid (HBF_4) has long been known as one of the low-damaging acid treatments for clayey sandstone formations, little is known of its chemistry which could explain the mixed results of fluoboric acid in actual field application. A better understanding of its limitations would contribute to an improved success rate in HBF_4 stimulation application.

The unique advantages of this acid system are the ability to reach deeper into formation to address damage at extended radius before spending, owing to its slow hydrolytic reaction to produce HF, as well as the stabilization and desensitization of undissolved fines with borosilicate.

A more comprehensive understanding of how the chemistry of fluoboric acid and its reaction products affect silica and aluminosilicates is crucial to the design and optimization of fluoboric acidizing treatment. Through a novel application of ^{11}B and ^{19}F Solution State High Field Nuclear Magnetic Resonance (NMR) spectroscopy, chemical complexes involved in the reaction were defined.

Various other experimental techniques were also employed in studies on the ability of hydrolyzed fluoboric acid to react with common clays found in sandstone at room and elevated temperatures, as well as coreflooding to investigate clay migration development. Analyzing fresh and spent acid with inductively coupled plasma (ICP) and ^{11}B and ^{19}F NMR helps identify reaction products and their distribution. A set of 12-3

mud acid experiments was done in parallel to serve as a reference to 3%- equivalent-HF fluoboric acid in aqueous-HCl solution.

NMR results show complex mixtures of fluoborate species from HBF_4 hydrolysis and products from HF-aluminosilicates reaction. The fresh HBF_4 hydrolysis study at room temperature has confirmed retarded HF generation with presence of BF_4^- and $BF_3(OH)^-$ and absence of $BF_2(OH)_2^-$ or $BF(OH)_3^-$ species . The effect of temperature on HBF_4 reaction has also been studied to validate functionality of acid at 75°F and 200°F. A series of lab dynamic flow testing in Berea sandstone corroborates conclusions from lab experiments by showing decrease in permeability when treating Berea sandstone cores with HBF_4 at 200°F. Fluoboric acid treatment is therefore not suitable for formations with approximate temperature of 200°F.

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NOMENCLATURE

DIW	Deionized water
HF	Hydrofluoric Acid
HCl	Hydrochloric Acid
HBF_4	Fluoboric Acid
PV	Core Pore Volume
ACS	American Chemical Society
ASTM	American Society for Testing and Materials
md	Millidarcy
CEC	Cation Exchange Capacity
wt%	Weight Percent
rpm	Revolutions per Minute

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Background

Hydrofluoric acid (HF)-hydrochloric (HCl) acid mixtures, or mud acid, have been used to stimulate sandstone reservoirs since the 1930s. Use of mud acid treatment can include fracturing operations, acidizing operations, scale removal, drilling operations or even sand control operations.

Most sandstone formations consist primarily of quartz or sand particles bonded together by cementing materials which are typically calcite ($CaCO_3$), silicates and aluminosilicates (clay and feldspar). While most carbonate formations can be effectively treated with various mineral acids or organic acids relying on the acidity of treatment fluid, siliceous formations are not noticeably reacted by the same mechanism. The most common method of treating sandstone formations is to introduce an acid system comprised of HF into the target formation. The HF component is recognized specifically for its first order reaction with aluminosilicates (Smith and Hendrickson 1965) as a function of mineral surface area, removing aluminosilicates from the conductive flow path. HF can dissolve clays, feldspar, quartz, micas and chert, but the primary objective is to remove clays. Reactions of HF with indigenous clay and siliceous matrix in sandstone are complex and vary from one formation to another, depending on which types of clay it contains. Reactivity of different clays with HF has been investigated by Gdanski (Gdanski 1999, Gdanski 1998) and Hartman et al (Hartman et al. 2006). The

use of low pH fluid can cause higher mineral dissolution which further induces adverse effects in certain instances, especially the precipitation of dissolved fluoride with group 1 metal ions (Na^+ and K^+), group 2 metal ions (Mg^{2+}, Ca^{2+}, and Ba^{2+}), and Al^{3+} (Reyes 2012). An HCl preflush sequence can be applied to dissolve carbonate minerals as much as possible before HF will be pumped to treat clay at a later stage.

The reaction of HF with quartz is expressed in eq. 1

$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O \quad (1)$$

The primary reaction of HF and aluminosilicates according to Gdanski is:

$$(5 + x)HF + M\text{-}Al\text{-}Si + (3 - x + 1)H^+ + H_2O \rightarrow HSiF_5 + AlF_x^{(3-x)+} + M^+ + H_2O \quad (2)$$

Where x is F/Al ratio and M^+ is all other cations, such as Na or K. This reaction will completely dissolve aluminosilicates and generate only soluble products. This is the only reaction that removes clay damage hence greatly improving permeability.

Fluorosilicates can be especially problematic because redissolution can be difficult. Fluoroaluminates are thought to be soluble as long as the pH is below about 2 and the F/Al ratio is maintained below about 2.5 (Shuchart and Gdanski 1996). If precipitated, their dissolution typically requires strong hydroxide concentration of more than 5%.

$HSiF_5$ or fluosilicic acid is capable of reacting further with aluminosilicates, therefore being referred to as the secondary reaction (eq. 3).

$$\frac{x}{5}HSiF_5 + M\text{-}Al\text{-}Si + (3 - x + 1)H^+ + H_2O \rightarrow AlF_x^{(3-x)+} + M^+ + silica\ gel \quad (3)$$

The secondary reaction dissolves all other portions of clays except for Si from the structure of aluminosilicates, leaving amorphous silica gel film in place. This process is found to be significantly fast and go to completion at temperature above 125°F (Gdanski 1999). The reaction rate is much slower at any temperature below that.

The tertiary reaction occurs when aluminum fluoride complexes react with clays, continuing to reduce the F/Al ratio in the spent HF until all remaining H^+ is consumed (eq. 4).

$$yAlF_x^{(3-x)+} + (x - y)Al\text{-}Si + 3(x + y)H^+ \rightarrow xAlF_y^{(3-y)+} + silica\ gel \quad (4)$$

The fluoride number coordinated with aluminum before tertiary reaction (x) is more than that after reaction (y). The tertiary reaction rate was found to be very slow below 200°F(Gdanski 1998).

A literature review has indicated at least two distinct drawbacks of traditional mud acid in stimulating sandstone formations. Firstly, at certain reservoir temperatures, the rapid reaction of HF with siliceous materials, specifically clay, deter the penetration capacity of acid into the formation. It is generally believed that mud acid removes skin damage from only the first few inches around the wellbore (McBride et al. 1979).

Another reason is early production decline soon after the formation has been stimulated, resulting from pore throat plugging by migratory clays and other fines (Thomas and Crowe 1978), exacerbating formation deliverability to even lower than pre-treatment level. Severe loss of permeability in sandstones due to authigenic clay

migration in response to mechanical forces or water salinity changes was found to induce total pore plugging even in sandstone of 500 milli-darcy initial permeability (Gray and Rex 1990).

Fluoboric Acid

Fluoboric acid (HBF_4) is a water unstable compound of which extent of hydrolysis is markedly dependent on temperature and acid concentration. The slow hydrolytic reaction gradually releases hydrofluoric acid to its environment. The hydrolysis reaction of fluoboric acid at room temperature has been investigated in detail (Wamser 1948, 1951).

By nature, aqueous solutions of fluoboric acid will be hydrolyzed at a degree which depends on acid concentration, temperature, and standing time after preparation (Ryss 1956) as well as HF/ H_3BO_3 molar ratio in the starting mixture (Radosavljević et al. 1979). The hydrolysis constant of BF_4^- at various conditions had been determined from pH data by Ryss and Bakina according to the equilibrium hydrolysis of the BF_4^- ion corresponding to the following reactions, with the assumption that BF_3OH^- and BF_4^- are completely dissociated and no HF_2^- formed:

$$BF_4^- + H_2O \rightleftharpoons BF_3OH^- + HF \quad (5)$$

$$HF \rightleftharpoons H^+ + F^- \quad (6)$$

$$Degree\ of\ hydrolysis, k = \frac{[BF_3OH^-][HF]}{[BF_4^-]} \quad (7)$$

The degree of hydrolysis of HBF_4 increases with an increase in temperature or an excess amount of boric acid present but decreases with increasing acid concentration or an excess amount of HF present (Wamser 1948). At room temperature, only around 8-10% of HBF_4 will hydrolyze and yield available HF to react with clay. When HF is consumed, the equilibrium will shift to the right causing more BF_4^- to hydrolyze and produce a substitute amount of HF to maintain its constant level. The limited HF availability at any given time has made HBF_4 hydrolysis the control process when comparing to the mud acid spending rate on aluminosilicates. This is usually called a retarded HF acid system.

In 1978, Thomas and Crowe introduced the use of fluoboric acid in treating sandstone reservoirs. It was found to be very effective in increasing live acid penetration and stabilizing undissolved clays to the sand grain with borosilicate (Thomas and Crowe 1978, Thomas et al. 1978). During the fixing process, aluminum will be extracted from clays and exchanged with boron to produce borosilicate material. Due to its retarding feature, HBF_4 could dissolve clays as effectively as mud acid but at a much slower rate. Therefore, to adequately address the damage, HBF_4 acid is usually designed as a postflush to mud acid.

The aqueous fluoboric acid used in this experiment was prepared by treating ammonium bifluoride with stoichiometric amounts of boric acid and hydrochloric acid.

$$2NH_4HF_2 + H_3BO_3 + 2HCl \rightleftharpoons 3H_2O + HBF_4 + 2NH_4Cl \quad (8)$$

Fluoboric acid will not form in the mixture immediately after preparation (Wamser 1948). At this stage, the total titratable acidity corresponds to 5 equivalent of

acid and leaves F^- and BO_2^- anions at the end point of titration. Fluoboric acid content will gradually increase in solution over time to equilibrium levels while total acidity decreases to a certain value. At titration end point, the solution will contain additional BF_4^- ions compared to those mentioned above. These phenomena are represented by a 2-step chemical reaction (Travers 1930):

(Fast reaction) $$H_3BO_3 + 3HF \rightarrow HBF_3OH + 2H_2O \quad (9)$$

(Slow reaction) $$HBF_3OH + HF \rightleftharpoons HBF_4 + H_2O \quad (10)$$

Hydrogen ions catalyze the formation of HBF_4. The rate of reaction of HBF_3OH with HF depends essentially on the acidity of the solution. Hydrolysis of HBF_4 is also catalyzed by Ca^+ ions (Ryss 1956).

Alkali salts of BF_4^- are much less soluble than those of BF_3OH^- (Ryss 1956), and are likely to precipitate out of solution. This is due to the fact that the replacement of the F^- ions by the OH^- ions leaves the lattice energy unchanged but increases the hydration of the anion. KBF_4 is one of the least soluble fluoborate compounds.

BF_3OH^- is an acid anion of considerably greater strength than HF. Thus only in very dilute solutions (0.002M at 20°C) will further hydrolysis of HBF_3OH to $HBF_2(OH)_2$ occur (Ryss 1956). The assumption that this hydrolytic equilibrium is very rapidly established (in contrast to the slow hydrolysis of HBF_4) is further supported by the result of KBF_4 and KBF_3OH aqueous solution titration with thorium nitrate in the presence of alizarin red S, which suggested that none of the fluoride in BF_4^- is available but the fluorine in BF_3OH^- is rapidly and quantitatively available (Wamser 1951).

The observed decrease in acid strength in the order $HBF_4 > HBF_3OH > HBF_2(OH)_2 > HBF(OH)_3 > H_3BO_3$ may be explained by the changes in the electrostatic inductive effect of the anion on the proton as fluorine atoms are successively replaced by hydroxyl groups. The highly electronegative fluorine atoms attract electrons more strongly than oxygen atoms, so that the tendency for the proton is to be held more firmly by a B-linked OH group than by B-F unit (Wamser 1951).

The HBF_4 acid system used in this study is similar to that used in a study by Al-Dahlan et al (Al-Dahlan et al. 2001).

NMR analysis is the main research technique used in this study. This technique exploits the magnetic properties of certain atomic nuclei in a magnetic field which absorb and re-emit electromagnetic radiation that resonates with the intramolecular magnetic fields around an atom. The spectrum obtained can then provide detailed information about the structure, dynamics, reaction state, and chemical environment of molecules, which can be used to confirm the identity of a substance. ^{11}B and ^{19}F NMR have never before been used to study the HBF_4 acid reaction with clay and sandstone.

Literature Review

In 1948, Wamser studied the hydrolysis of fluoboric acid in aqueous solution and found that when mixing 4 moles of HF acid with 1 mole of boric acid in aqueous medium, 3 moles of HF will react immediately to form HBF_3OH. Then, the remaining HF will react slowly with HBF_3OH to gradually form HBF_4 until equilibrium is reached (Wamser 1948). The equilibrium constant of 0.1105 M fluoboric acid at 25°C has been

determined to be 2.3×10^{-3}. It was noted that the prepared solution contains no HBF_4 immediately after preparation and that hydrolyzed aqueous fluoboric acid solutions do not contain any free boric acid. From conductivity titration, it was believed that an appreciable amounts of $HBF_2(OH)_2$ and $HBF(OH)_3$ also exist at their reversible equilibrium with HBF_3OH (Wamser 1948).

Fluoboric acid or clay acid, had later been employed in field application to stimulate and control clay in a sandstone formation by Thomas and Crowe in 1978 (Thomas and Crowe 1978, Thomas et al. 1978). Clay acid was proven to be effective in providing deeper live acid penetration and minimizing clay swelling and migration through chemical fusion of clay platelets from the borosilicate formation when HBF_3OH reacts with siliceous material. Tests showed that HBF_4 has an ability to reduce the CEC of bentonite up to 93%. In order to achieve these features of clay acid, a shut-in period following acid injection is required as the decrease in clay swelling is a function of time. The shut-in period varies from 30 minutes at 300°F to 96 hours at 100°F for the cores used in this study. Mud acid generally precedes clay acid to remove surface plugging, then a postflush with clay acid is used to attain deep penetration. A reaction rate comparison test between 12-3 mud acid and the equivalent HF generating capacity 12% HBF_4 on glass slides at 150°F reveals a 10 fold difference in rate. Another test performed on sandstone with kaolinite showed an identical dissolution effect between the HBF_4 system at 150°F after 2 hours and 12-3 mud acid at 75°F after 20 minutes.

In 1979, McBride et al. used fluoboric acid to treat clay and quartz fines in gas wells with gravel pack completions in offshore Louisiana (McBride et al. 1979). They

observed that there was no increased precipitation of hexafluorosilicates and other reaction products after long term HBF_4 exposure. All wells treated by HBF_4 showed removal of damage in both gravel pack, perforations, and effective wellbore area with a slower production decline after treatment.

In 1983, Kunze and Shaughnessy pointed out that at typical formation temperatures (150-200°F), a supposedly retarded HBF_4 system will spend at the same rate as mud acid (Kunze and Shaughnessy 1983). Furthermore, the effect of the added HCl on the solution acidity has catalyzed the reaction and caused more BF_4^- to hydrolyze at equilibrium. Experimental results indicated similar acid penetration in both Berea and actual formation corefloods across 2 acid systems. The stirred reaction experiments likewise confirmed no difference in acid-clay dissolution. No fresh water sensitivity existed in cores treated with conventional HF acid and cores treated with HBF_4. It was found that BF_4^- hydrolysis will increase with soluble aluminum concentration. Shutting in BF_4^- will lead to silica precipitation and possible pore plugging as much as if conventional HF were shut-in.

Laboratory work by Boyer and Wu in 1983 concluded that HBF_4 is suitable for clay bearing sandstones (Boyer and Wu 1983). Less silica precipitation was observed with HBF_4 than mud acid.

Bertaux adopted 8% HBF_4 acidizing in potassic mineral sandstone (containing K-feldspar and illite) in 1989 (Bertaux 1989) and concluded it enhanced permeability. Also the KBF_4 that was generated was non damaging. Meanwhile, the HF acid-mineral reaction led to K_2SiF_6 precipitation, resulting in a significant permeability reduction.

Moreover, silica and borosilicates formed during the shut-in period fused non-dissolved particles and provided permanent stabilization.

Ayorinde et al. (1992) applied HBF_4 in high rate oil and gas wells (cased or gravel packs) to prevent post treatment fines migration and to sustain production as an alternative to conventional clay control agents (cationic polymers) used in the overflush (Ayorinde 1992).

Paccaloni and Tambini used HBF_4 to treat a well with silt and clay damage resulting from mud acid treatment in 1993 (Paccaloni and Tambini 1993). Production was reported to plateau for 5 years following treatment.

Previous work by Shuchart (1995) used ^{19}F NMR spectroscopy to study aluminum and silicon fluorides equilibria and the reactions of HF acid and H_2SiF_6 on aluminosilicates (Shuchart and Buster 1995). During the secondary reaction of silicon fluorides with aluminosilicates, a constant F/Al ratio was maintained until the silicon fluorides had reacted completely. The distribution of fluoride species depends on the HCl concentration. When the silicon fluorides have reacted completely to give silica gel, the aluminum fluoride complexes continue to react on fresh aluminosilicates (tertiary reaction) and cause the aluminum content to increase (leaching more Al) and the F/Al ratio and acid concentration to decrease below 1. The final F/Al ratio is dependent upon acid strength and temperature. In wells with temperatures of 150 to 200°F, the reaction of H_2SiF_6 continued to completion. Silicon content was low and pH levels were 2 to 3. The F/Al ratios of the returns were 0.5 to 1.3, depending on the concentration of HCl and HF in the treatment.

In 1999, Kume et al. reported that the use of fluoboric acid to treat wells in Niger Delta returned mixed results, including some with unimproved or damaged permeability (Kume et al. 1999).

Al-Dahlan et al. (2001) studied retarded acid systems, one of which was HBF_4, against mud acid (Al-Dahlan et al. 2001). Observations from lab experiments are that HBF_4 does not react with quartz and was retarded only in the first 30 minutes when reacted with kaolinite and chlorite and 1 hour when reacted with illite and bentonite. HBF_4 had the weakest dissolving power for silicon. This system precipitated hydrated silica with increasing reaction time. HBF_4 precipitates KBF_4 when reacted with illite.

Jaramillo et al. introduced a blend of organic/fluoboric acid system in 2010 (Jaramillo et al. 2010). Organic acid acted as chelant to minimize precipitations. This acid was used as the main treatment acid, eliminating the HF preflush stage. Productivity improvement was evident after treatment and remained stable, indicating efficient fines control. It claimed to be effective in fines stabilization at all temperatures.

In 2011, Feng et al has developed a new sandstone acid formulation (HTDP, a chemically modified organo-phosphonic acid) that has proven better in enhancing permeability in lab formation coreflood than HBF_4 (Feng et al. 2011).

Field study in 2012 by Restrepo et al. used a system of organic acids - HBF_4 to obtain deep live acid penetration and to minimize secondary/tertiary reactions associated with the formation of scales, HCl sensitive asphaltenes, and oil wet fines problems (Restrepo et al. 2012). Organic acids chelate Al^{3+} ions, keeping silica from precipitating

as hydrated silica inside solution. Consequently, this leads to more aluminosilicates dissolving.

Reyes (2012) patented a treatment fluid that contained boron trifluoride complexes with chelating agents for use in formations with temperatures of at least 200°F (Reyes 2012). The boron trifluoride complex serves as a precursor of HF acid with an advantage of having higher pH (>2) than HBF_4, which lessens the risk of unwanted precipitation. Another advantage claimed by this system is that a number of different boron trifluoride complexes, having differential stabilities, may advantageously be utilized to control the release of HF acid at a desired time or location within the formation. HBF_4 solution is rapid in generating HF and other BF species, while the hydrolysis rate of boron trifluoride complexes is not as rapid. Furthermore, the ligands that complex with boron trifluoride and are released into treating fluid when boron trifluoride decomposes may enhance treatment in certain applications, e.g., solvents (alcohols and ethers), acids (phosphorus and acetic acid), or amines (methylamine and ethylamine).

In 2013, Gomaa et al. devised a one-step sandstone acid system that eliminates the HCl preflush/postflush stage (Gomaa et al. 2013). This acid system was composed of HBF_4, HCl, organic acid, acid retarder and clay control additives. Lab stimulation on Bandera sandstone cores at 180°F yielded permeability enhancement. It was discovered that increasing the HCl/HF ratio increased the permeability enhancement and reduced the acid volume needed. There is a minimum acid volume needed to achieve

permeability enhancement. This minimum PV depends on the HCl:HF ratio of the acid system and sandstone composition.

CHAPTER II

EXPERIMENTAL STUDIES

NMR analysis is the main research technique used in this study. This technique exploits the magnetic properties of certain atomic nuclei in a magnetic field which absorb and re-emit electromagnetic radiation that resonates with intramolecular magnetic field around an atom. The spectrum obtained can then provide detailed information about the structure, dynamics, reaction state, and chemical environment of molecules, which can be used to confirm the identity of a substance.

All ^{11}B and ^{19}F NMR spectra were recorded in $CDCl_3$ using a Varian Inova 400 MHz spectrometer. Chemical shifts for fluorine were recorded in parts per million (ppm, δ) relative to $CFCl_3$ using trifluorotoluene ($C_6H_5CF_3$, δ −63.72 ppm) as an internal standard. ^{11}B NMR shifts are reported in ppm relative to boron trifluoride etherate ($BF_3 \cdot OEt2$) as the external reference. Samples are contained in 5 mm OD borosilicate tubes lined with FEP NMR tube liners to prevent contamination from borosilicate glass. ^{11}B and ^{19}F NMR acquisition parameters are as shown in table 1.

^{19}F NMR Acquisition Parameters	^{11}B NMR Acquisition Parameters
○ Inova400 Brand, turned to 375.9 MHz ○ Run sample w/o internal lock signal in 5 mm OD tubes ○ Acquisition parameters ▪ Spectral width of 50,000 Hz ▪ 45 degree pulse angle ▪ 2 second relaxation delay ▪ 44 to 128 scans per data set,- depending on fluorine-concentration	○ Inova400 Brand, turned to 128.2 MHz ○ Run sample w/o internal lock signal in 5 mm OD tubes ○ Acquisition parameters ▪ Spectral width of 38,461.5 Hz ▪ 45 degree pulse angle ▪ 0.001 second relaxation delay ▪ 200 to 620 scans per data set,- depending on Boron-concentration

Table 1: NMR acquisition parameters.

Acid Used

Three different acid formulations are used in this research: 3% HBF_4, 8% HBF_4, and 12-3 mud acid. Both 3% and 8% HBF_4 are prepared according to eq (8). Due to the limited solubility of boric acid in high HCl content, the 8% HBF_4 solution contains no excess HCl.

The solutions were prepared using 18.2 MΩ•cm DIW, concentrated ACS grade HCl acid 36.5 wt% concentration, crystalized ammonium bifluoride, and powdered boric acid. Acids content are shown in table 2, 3, and 4.

	wt %
HBF_4	3.3%
HCl	12.0%
NH_4Cl	4.0%
H_2O	80.7%
	100.0%

Table 2: Content of 3% HBF_4 acid.

	wt %
HBF_4	8.0%
NH_4Cl	9.7%
H_2O	82.3%
	100.0%

Table 3: Content of 8% HBF_4 acid.

	wt %
HF	3.0%
HCl	12.0%
NH_4Cl	4.0%
H_2O	81.0%
	100.0%

Table 4: Content of 12-3 mud acid.

Clay Particle Size Selection

A sonic sifter with a series of sieves complying with ASTM E 11 standard, from top to bottom: 212 μm, 150 μm, 106 μm, 90 μm, 75 μm, and 45 μm were used to separate dry powdered clay as received from Ward's Science. Kaolinite and bentonite have a non-normal distribution for available sieve size ranges (Fig. 1 and 2). Particles

with diameters between 32-45 μm were selected to represent kaolinite and bentonite samples in this study, as this range is likely the mode of the size variation.

Illite samples were received in cobble sizes. They were broken down to final sizes using a rock grinder and a shatter box. Its particle distribution histogram appeared to be a normal-right skewed pattern, and is shown in Fig. 3. The particle diameters ranging from 90-106 μm were selected to represent illite.

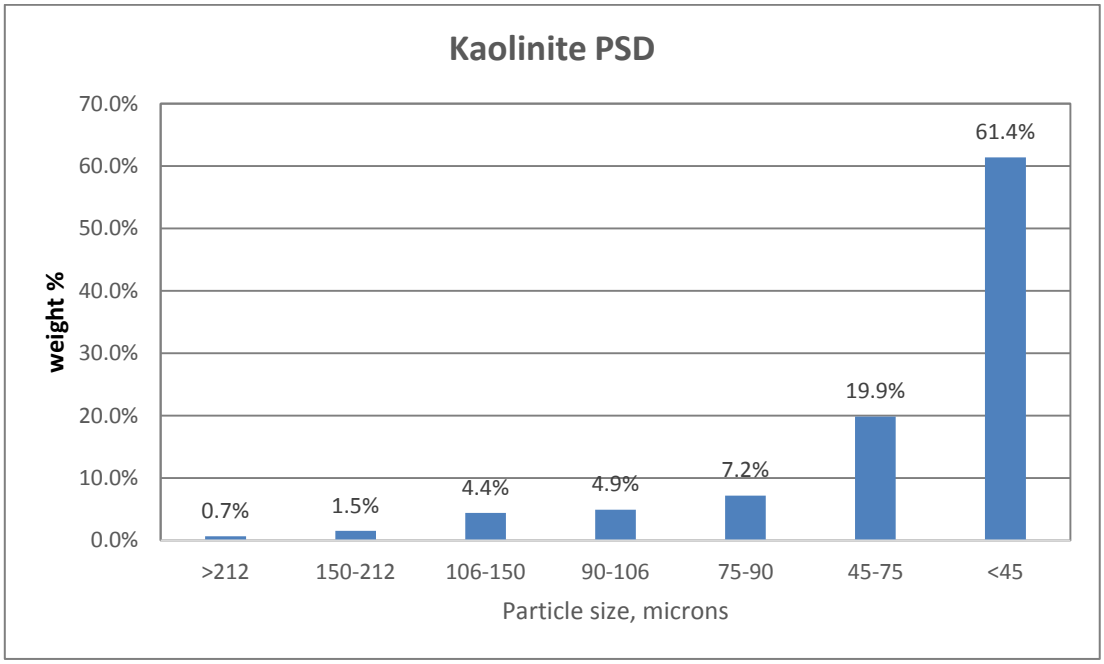

Figure 1: Kaolinite particle size distribution histogram.

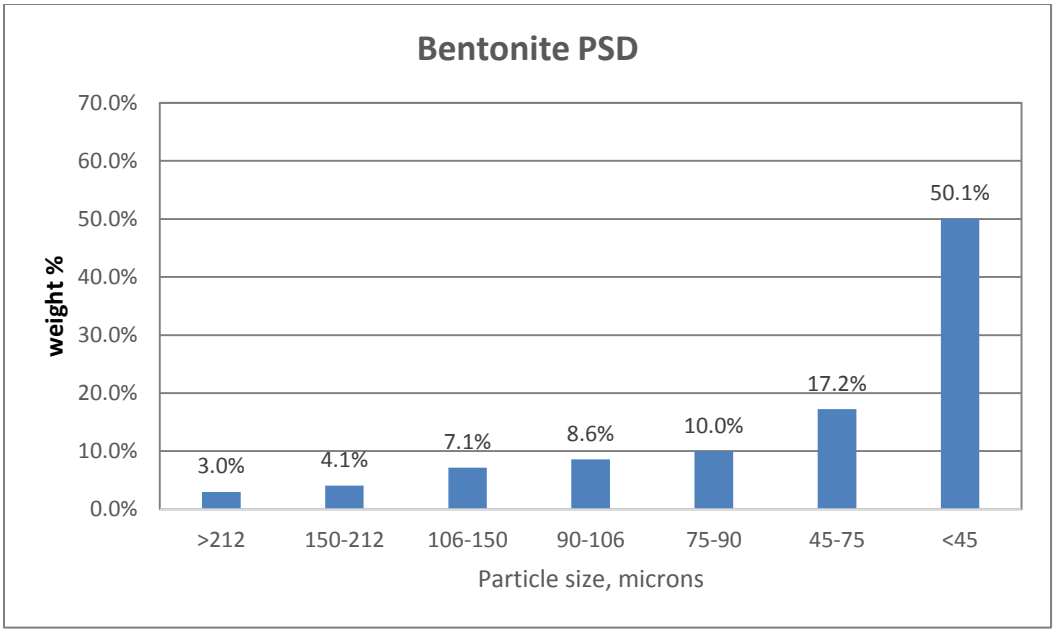

Figure 2: Bentonite particle size distribution histogram.

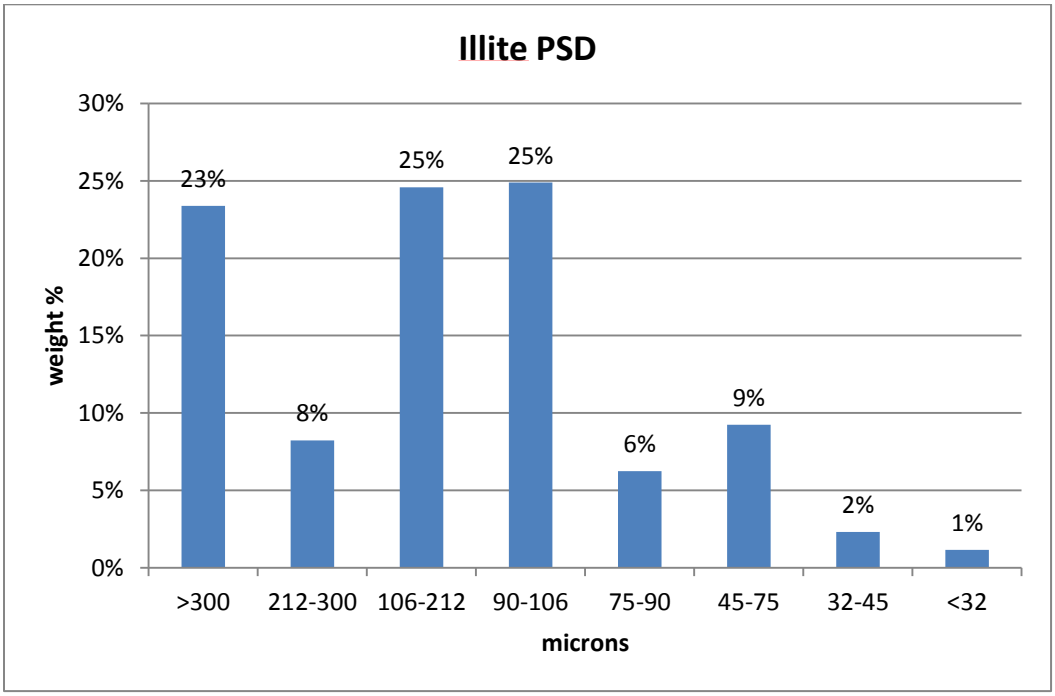

Figure 3: Illite particle size distribution histogram.

HBF_4 Hydrolysis Investigation with ^{11}B and ^{19}F NMR

To understand the extent of the hydrolysis process of HBF_4 and the fluoride distribution, a sample of 12% HCl-3% HBF_4 at 75°F was analyzed by ^{11}B and ^{19}F NMR at different times after acid preparation and the results will be compared to determine HF development in the system. Fig. 4 below is a sample spectrum of a different HBF_4 acid concentration showing the fluoborate ion as the predominant species present (Reyes 2012).

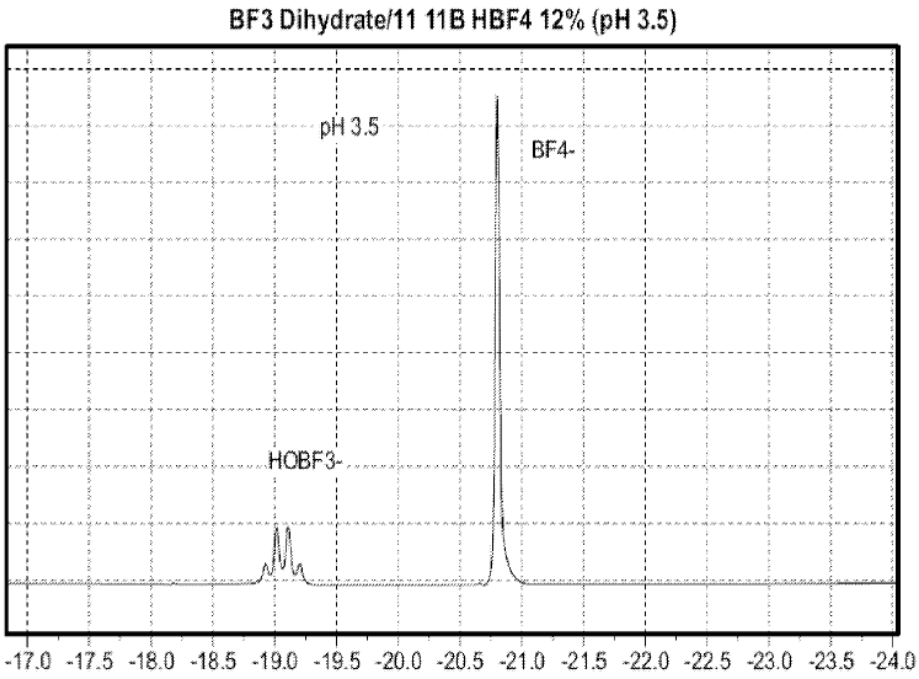

Figure 4: A sample spectrum of a different HBF_4 acid concentration.

Clay Dissolution Test at 75°F

This experiment is conducted to investigate the mechanisms which affect the dissolution behavior of kaolinite, bentonite and illite in aqueous fluoboric acid compared to aqueous hydrofluoric acid at 75°F. Four grams of each clay, sieved to control particle sizes and dried in an oven to remove excess water, is mixed with 40 g of 12% HCl-3% HBF_4 or 12% HCl-3% HF and allowed to react for 0.5, 1, 1.5, 2, 3 and 4 hours on a magnetic stirrer plate. When reaction time had elapse, the mixture was centrifuged at 6000 rpm for 2 minutes to separate live acid from clay, preventing further reaction. Quantitative grade filter paper was then used to separate the supernatant from the undissolved clay.

Clay weight loss percentages were recorded along with solution pH and free fluoride ion levels using a Cole-Parmer Fluoride Ion Electrode. The concentrations of key ions in these acids, aluminum, boron, phosphorus, silicon, calcium, magnesium, sodium, potassium, and total iron concentrations, were measured by Inductively Coupled Plasma Spectroscopy (ICP-OES). Dry clays and any precipitates were analyzed with an Evex Mini-SEM/EDS NanoAnalysis. Finally, the supernatant acid solution corresponding to 4 hours reaction time was analyzed by ^{11}B and ^{19}F NMR.

Clay Dissolution Test at 200°F

This experiment was conducted to investigate the mechanisms which affect the dissolution behavior of kaolinite, bentonite, and illite in aqueous fluoboric acid compared to aqueous hydrofluoric acid at 200°F, which could be considered normal

formation temperature. The experiment design was such that the secondary reaction of HF goes to completion.

Using the same clay as the 75°F test, 10 g of each clay is mixed with 100g of 12% HCl-3% HBF_4 or 12% HCl-3% HF and 1% vol corrosion inhibitor. The mixture was then contained in an OFITE aging cell (shown in Fig. 5), pressurized with nitrogen to 300 psi, and placed in rolling oven that was heated up to 200°F. The reactions were allowed to continue for 1,3 and 6 hours. When the reaction time has elapsed and the cell had cooled, the mixture was centrifuged at 6000 rpm for 2 minutes to separate live acid from clay, preventing further reaction. Quantitative grade filter paper was then used to separate the supernatant from the undissolved clay.

Clay weight loss percentages were recorded along with solution pH and free fluoride ion levels using a Cole-Parmer Fluoride Ion Electrode. The concentrations of key ions in these acids, aluminum, boron, phosphorus, silicon, calcium, magnesium, sodium, potassium, and total iron concentrations were measured by Inductively Coupled Plasma Spectroscopy (ICP-OES). Dry clays and any precipitates were analyzed with Evex Mini-SEM/EDS NanoAnalysis. Finally the supernatant acid solution corresponding with 6 hours reaction time was analyzed by ^{11}B and ^{19}F NMR.

Figure 5: OFITE aging cell.

Berea Sandstone Coreflood at 200°F

Berea sandstone is the most commonly used media in studying core flow test due to its homogeneity, which is favorable in control experiments, as well as its high permeability and porosity, resembling a good reservoir. The samples used had permeabilities ranging from 100-200 md.

Core flow tests were conducted using Berea sandstone cores of 1" diameter and 6" length saturated with 5 wt% NH_4Cl before use. A confining pressure of 2000 psi and a back pressure of 1000 psi were applied. The core temperature was stabilized at 200°F. Flow rates of 3-5 ml/min were employed. Effluent samples were collected at regular intervals and were later analyzed with Inductively Coupled Plasma Spectroscopy (ICP-OES) for key elements concentration and ^{11}B and ^{19}F NMR. A shut-in period of 1 hour

was incorporated in each test to allow for in situ HF generation and reaction from HBF_4. Coreflood pumping sequences are as shown in table 5.

Pressure drop across the core was recorded and plotted against pump schedule to track permeability change in the core when different fluids were pumped through. Initial and final permeability were calculated and compared.

Coreflood Pumping Sequences in Berea Sandstone	
	Pump 5 wt% NH_4Cl at 3 and 5 ml/min. Allow for pressure stabilization then measure initial permeability. Heat up the core to 200°F while pumping 5 wt% NH_4Cl at 1 ml/min.
Preflush	5 wt% HCl + 1 vol% corrosion inhibitor, 5 PV at 3 ml/min
Main acid	a) 3% HBF_4, 2 PV at 3 ml/min then shut-in for 1 hour. b) 8% HBF_4, 2 PV at 3 ml/min then shut-in for 1 hour. c) 12-3 mud acid + 1 vol% corrosion inhibitor, 2 PV at 3 ml/min
Postflush	5 wt% NH_4Cl, 5 PV at 3 ml/min
	Cool down the system to room temperature while pumping 5 wt% NH_4Cl at 1 ml/min Pump 5 wt% NH_4Cl at 3 and 5 ml/min. Allow for pressure stabilization then measure final permeability.

Table 5: Coreflood pumping sequences in Berea sandstone.

CHAPTER III

RESULTS AND DISCUSSION

HBF_4 Hydrolysis Investigation with ^{11}B and ^{19}F NMR

Fig. 6 shows the ^{11}B NMR spectra of fresh HBF_4 acid at t = 0, t = 30 minutes, t = 24 hours after preparation at 75°F. It appeared that only 2 species existed at all times. The sharp singlet at δ = –1.8 ppm is tetrafluoroborate (BF_4^-) and a quartet at around δ = -1.4 ppm is hydroxyfluoborate $BF_3(OH)^-$ (Prakash et al. 2011). The fluoborate ion is the predominant species present. Both species reach equilibrium very fast and maintain their levels past 24 hours.

The plot reveals that BF_4^- is formed instantly after HBF_4 acid was prepared at this H^+ concentration and that HF was readily available in the system at equilibrium. The plots also demonstrated that further acid decomposition to $HBF_2(OH)_2$ would not noticeably progress in the absence of material to react with.

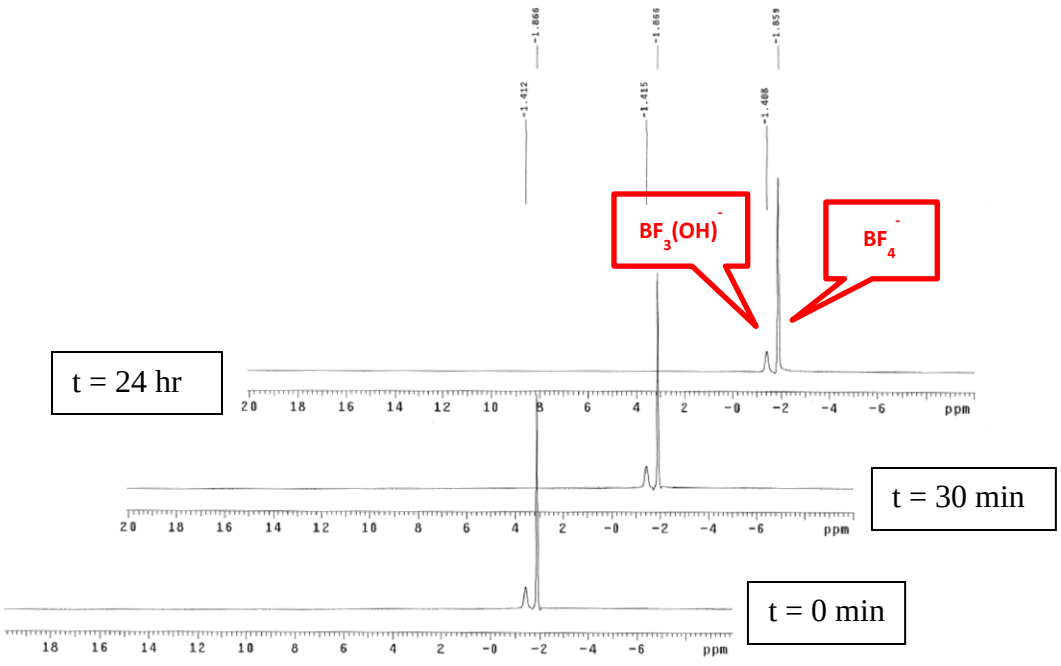

Figure 6: ^{11}B NMR spectra of fluoboric acid at different times after preparation.

Fig. 7 shows the ^{19}F NMR spectrum of fresh HBF_4 acid at t = 0 at 75°F. Two distinct species are BF_4^- at δ = -150 ppm and $BF_3(OH)^-$ at around δ = -147 ppm (Prakash et al. 2011). A third minor amount of fluoride containing species was also formed. Based on the chemical shift δ = -162 ppm, this is believed to be HF (Dungan and Van Wazer 1970). This reveals that HF is readily available in the acid solution once prepared but at a very limited quantity.

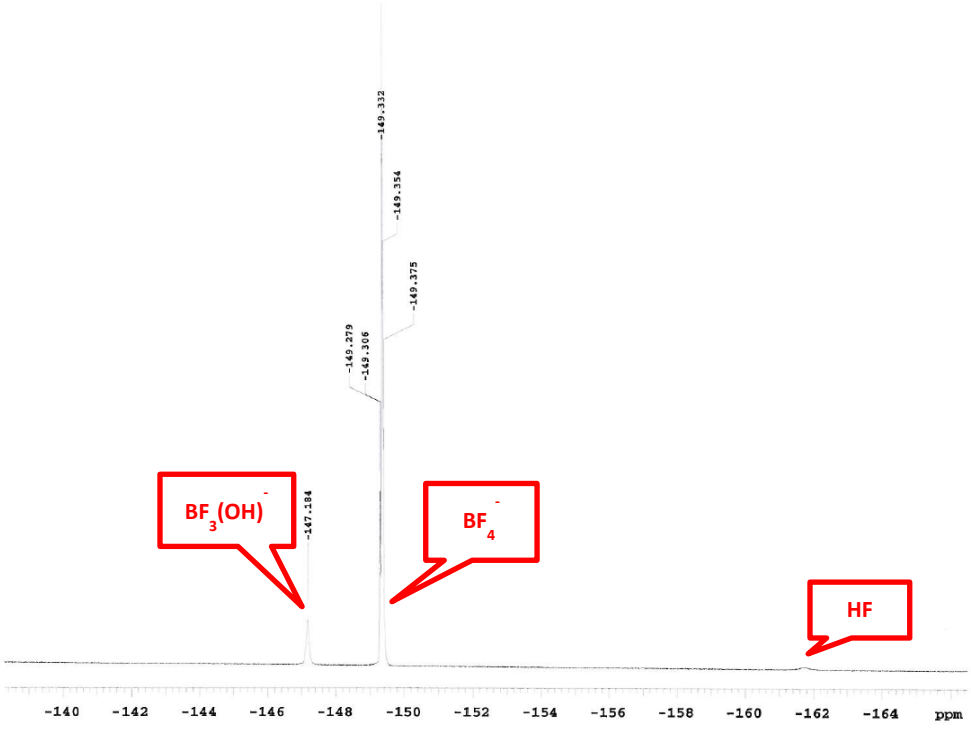

Figure 7: ^{19}F NMR spectra of fluoboric acid immediately after preparation.

Clay Dissolution Test at 75°F

Comparing Fig. 8 and Fig. 9, the retardation effect of 3% HBF_4 at room temperature is up to 60% of the conventional mud acid reaction rate for kaolinite and illite. For bentonite, the retardation of HBF_4 went up as high as 80-90%.

Fresh clays and clays which were dissolved by HBF_4 for 4 hours at 75°F were analyzed by SEM-EDS and compared side by side in Fig. 10. Each clay's Al/Si ratio before and after HBF_4 dissolution remains almost constant, maintaining their structural properties of 1:1 (kaolinite) clay or 2:1 (illite and bentonite) clay. HBF_4 can then be

assumed to attack the tetrahedral silicate sheet and octahedral aluminate sheet equivalently.

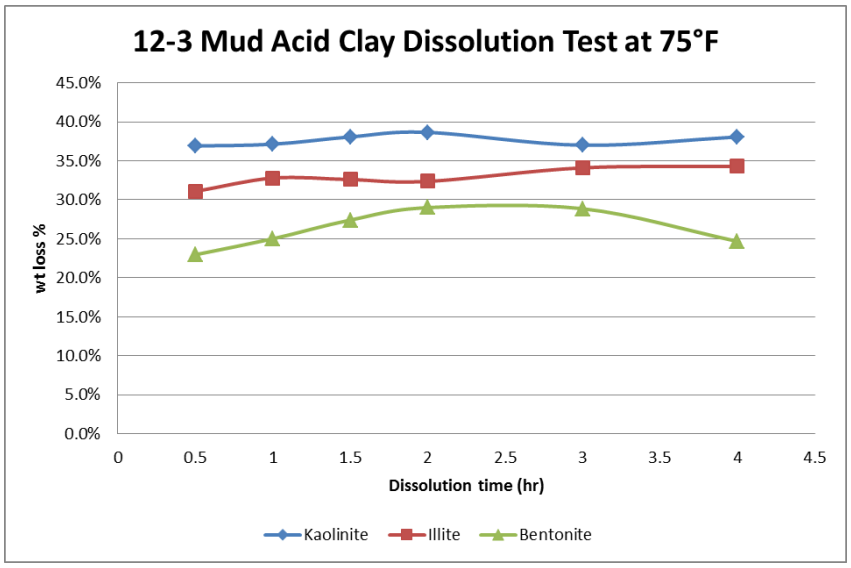

Figure 8: Clay weight loss % for mud acid dissolution test at 75°F.

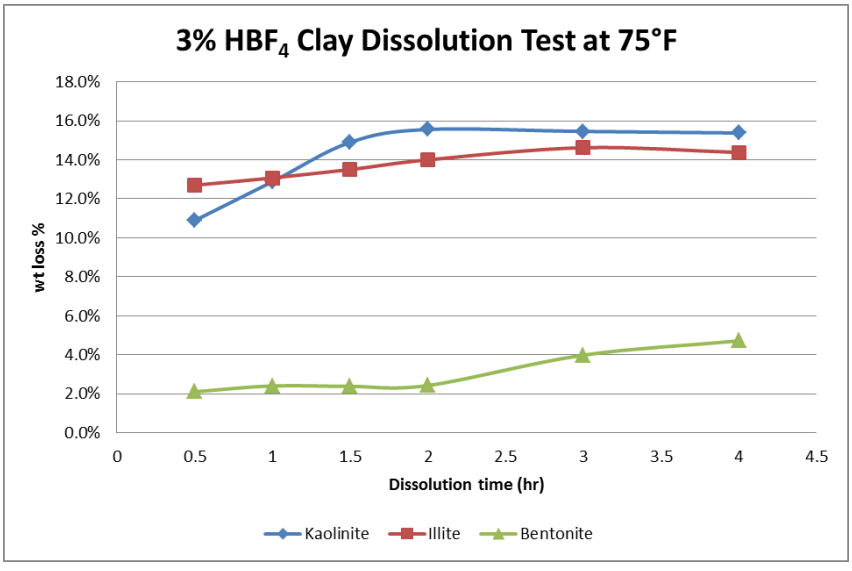

Figure 9: Clay weight loss % for 3% HBF_4 dissolution test at 75°F.

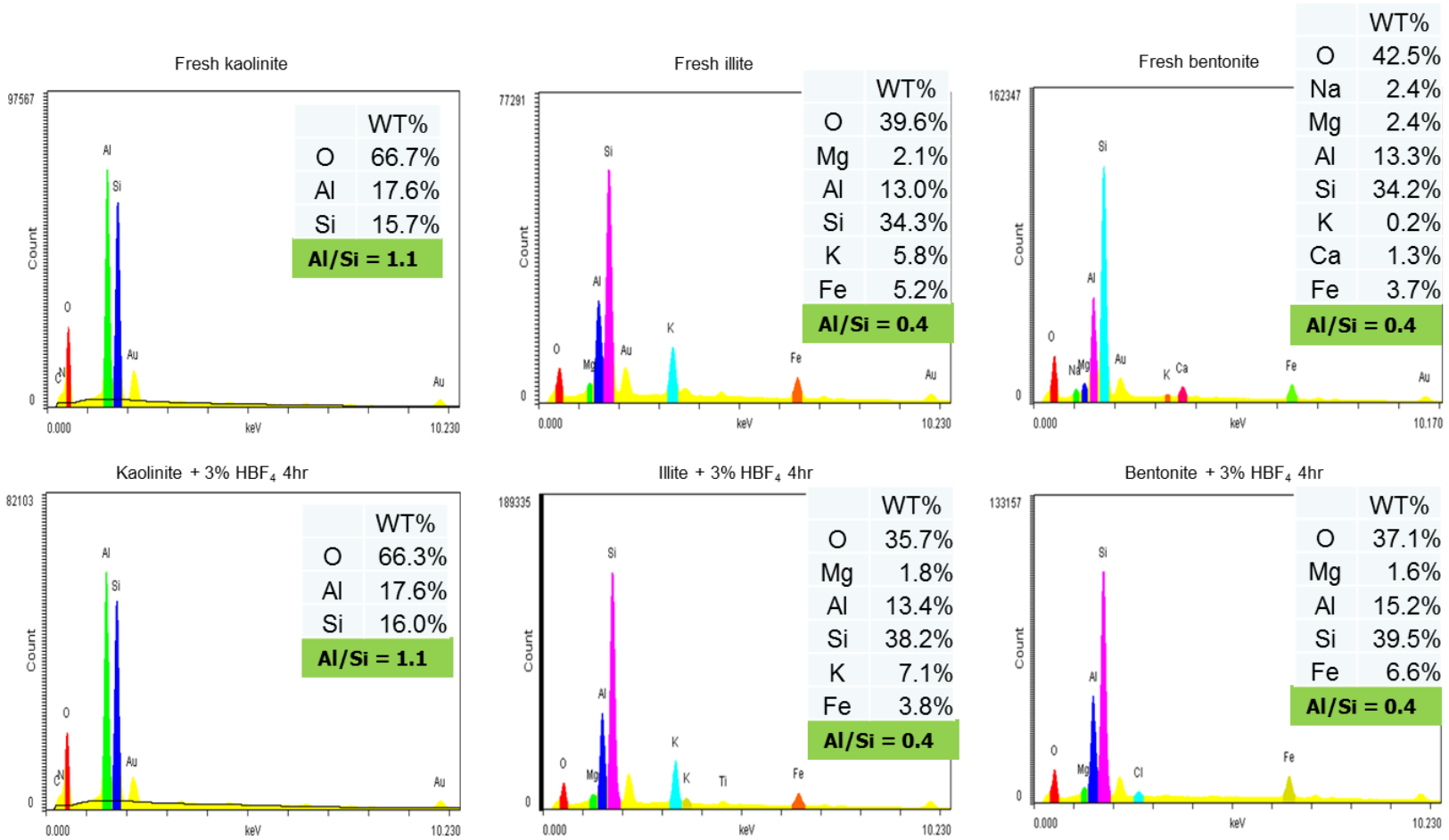

Figure 10: EDS spectra of fresh clays (top row) vs 3% HBF_4 dissolved clays at 75°F for 4 hours (bottom row).

Fig. 11-13 show boron concentration in the supernatant of 3% HBF_4 reacted with clays at 75°F for 4 hours. Among all 3 clays, only illite shows a decreasing level of boron in solution. Traces of white precipitate were also observed lying on bottom of the test tubes. This precipitate was filtered out of solution, washed with DIW, dried, and sent for X-Ray diffraction (XRD) analysis. Result confirms existence of KBF_4. No precipitate was observed with kaolinite or bentonite.

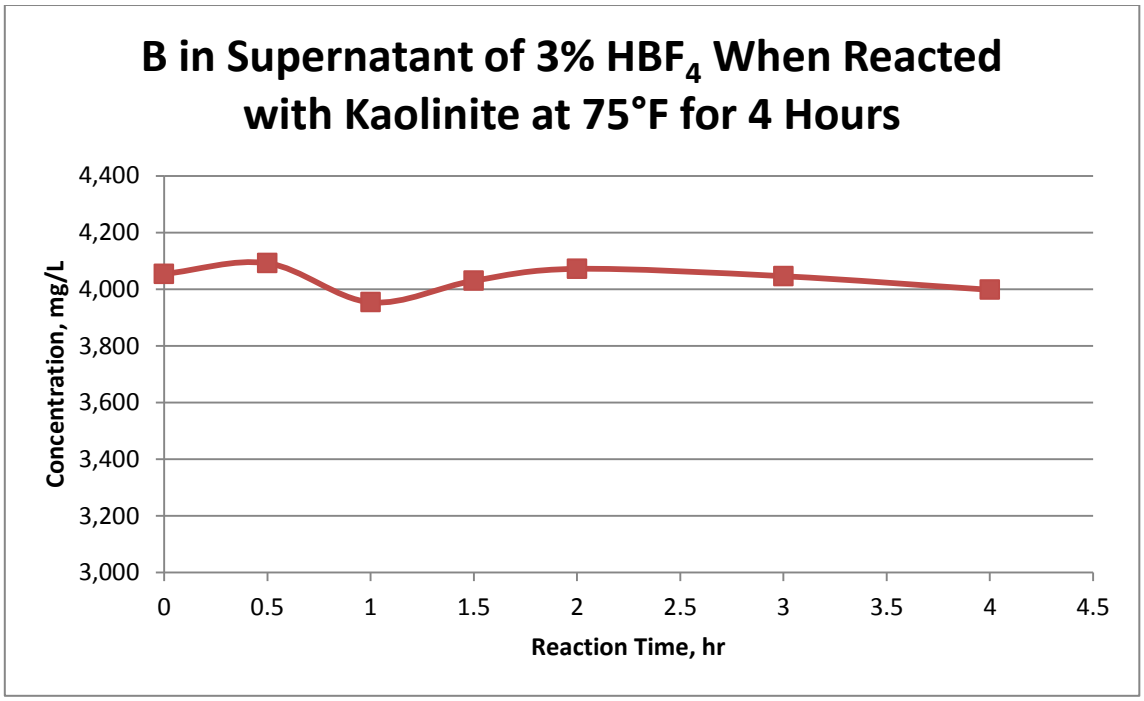

Figure 11: Boron concentration in supernatant of 3% HBF_4 reacted with kaolinite at 75°F for 4 hours.

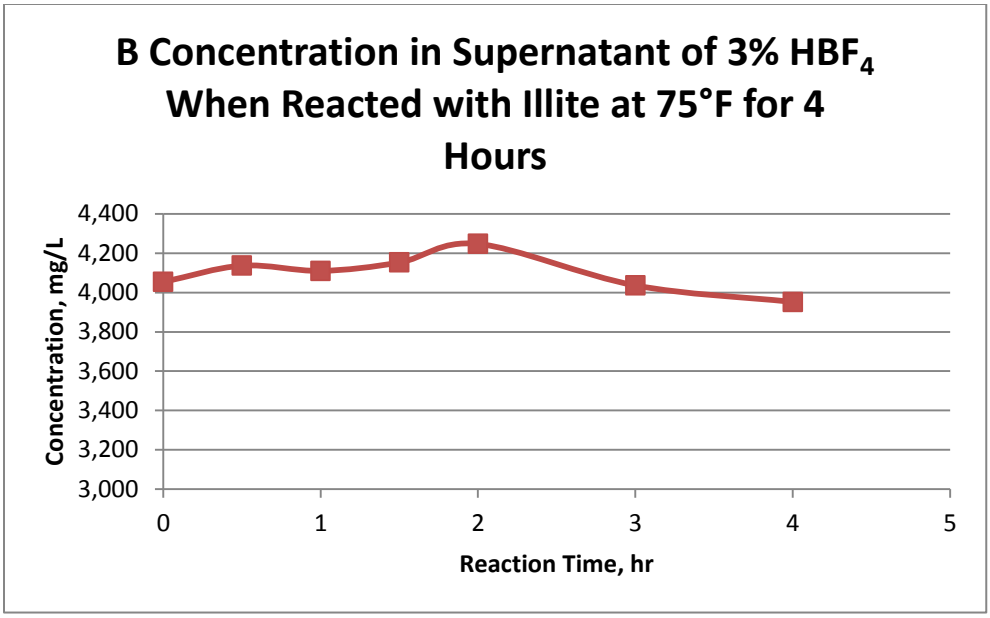

Figure 12: Boron concentration in supernatant of 3% HBF_4 reacted with illite at 75°F for 4 hours.

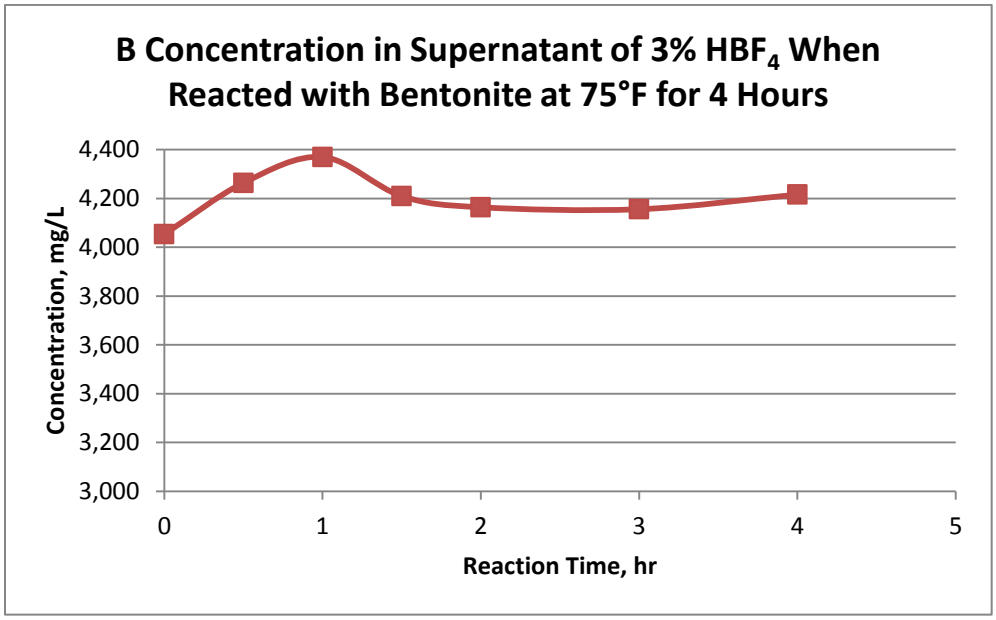

Figure 13: Boron concentration in supernatant of 3% HBF_4 reacted with bentonite at 75°F for 4 hours.

In Fig. 14, while all other key elements except Ca are reflecting the retarded reaction of HBF_4, potassium concentration extracted by HBF_4 is at around five times of that extracted by mud acid. Fig. 15 shows the ^{19}F NMR spectrum of 12-3 mud acid reacted with kaolinite for 4 hours at 75°F.Two species can be identified as silicon fluoride (SiF_y) at δ=-129 ppm and aluminum fluoride ($AlF_x^{(3-x)}$) at δ=-155-156 ppm. Comparing this spectrum with Fig. 16, two expected additional species appeared at δ=-145 ppm, which was assigned as BF_3OH^- and δ=-150 ppm, which was assigned as BF_4^-. A spectrum in Fig. 16 has smaller intensity at both the SiF_y peak and the $AlF_x^{(3-x)}$ peak when compared to Fig. 15. This reflects the retardation effect of HBF_4. The $AlF_x^{(3-x)}$ peak in Fig. 17 has diminished to a very low level comparing to kaolinite due to less Al available to complex with F^- (see Fig. 18).The reason that a ^{19}F NMR spectrum in Fig. 19 only shows BF_3OH^- at δ=-147 ppm and BF_4^- at δ=-149 ppm is probably because the very low dissolution rate provided a limited amount of Si and Al from bentonite to complex with F^-. The peaks then become unnoticeable.

Three species of boron containing compounds were found in ^{11}B NMR spectra of reacted 3% HBF_4 with clays (Fig. 20-22). A peak at δ=19 is assigned as H_3BO_3 (Dewar and Jones 1967), a peak at δ=0 is assigned as BF_3OH^- and the last peak at δ=-2 is assigned as BF_4^-. None of the spectra show the $BF_2(OH)_2^-$ or $BF(OH)_3^-$ species since BF_3OH^- is rapidly converted to a less fluorinated borate in water to its final form (H_3BO_3). In Fig. 21-22, the spectra got cut off before the range of boric acid. This is probably due to a very a low boric intensity since these systems are retarded more than kaolinite.

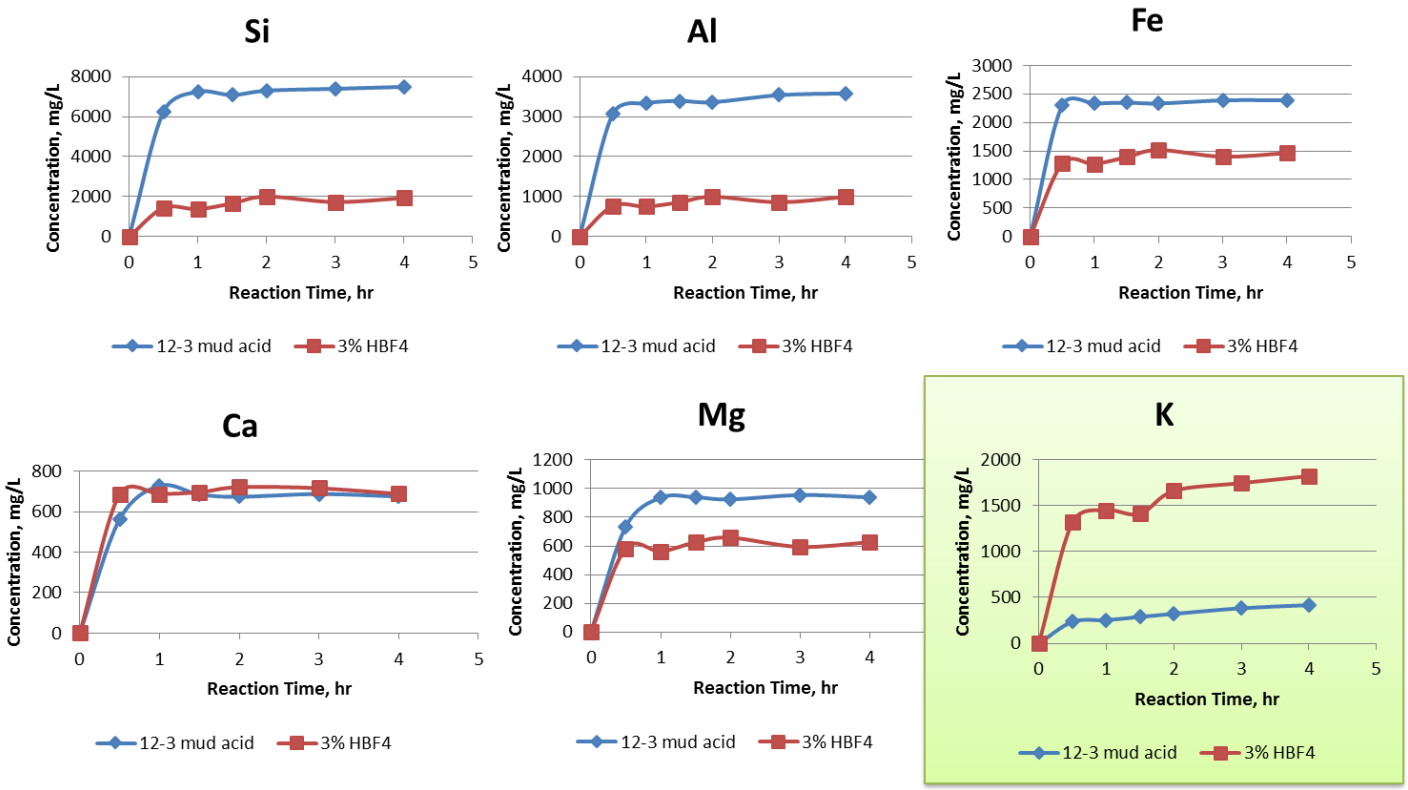

Figure 14: Key elements in solution of illite + 12-3 mud acid and 3% HBF_4 at 75°F.

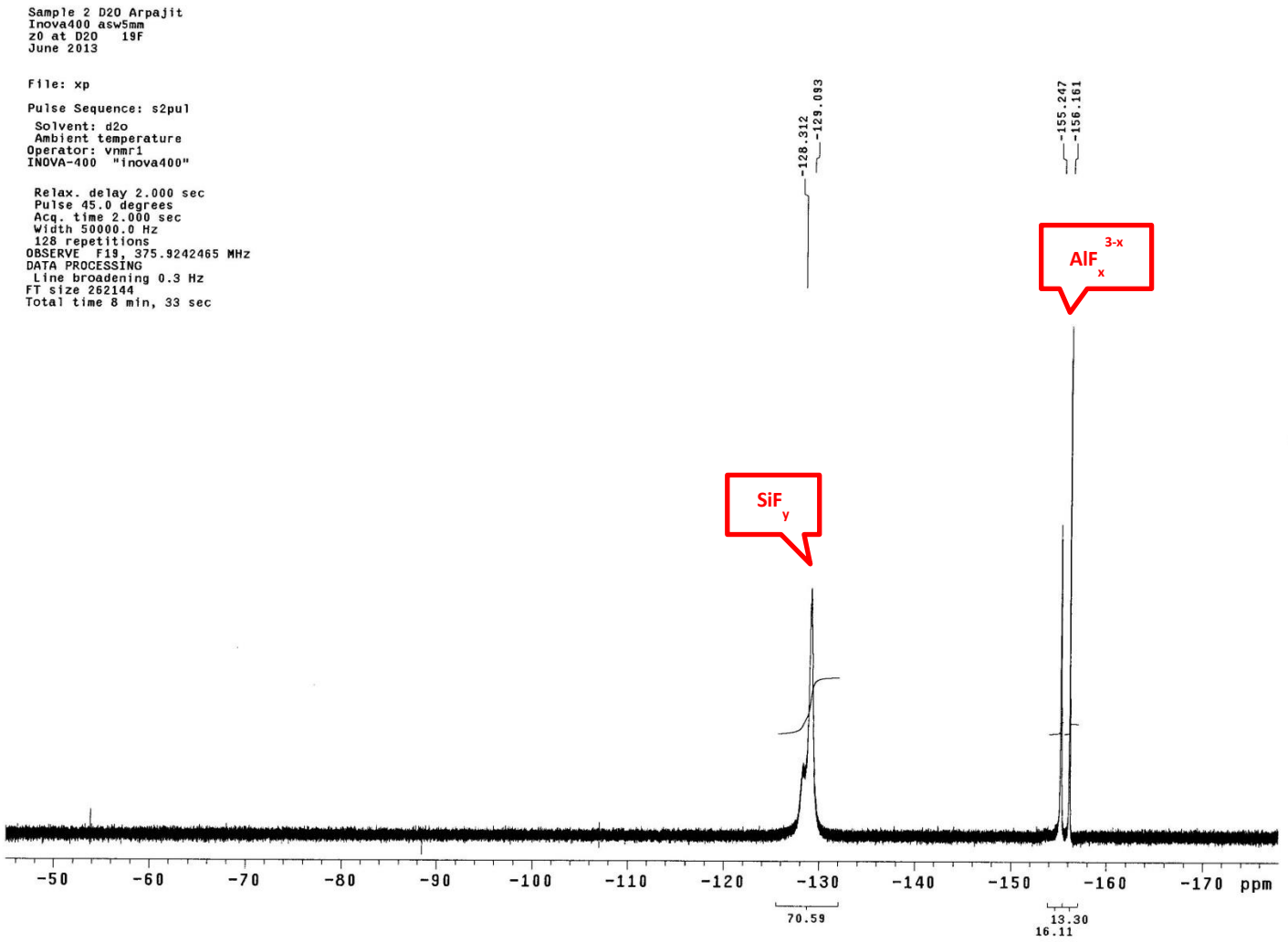

Figure 15: ^{19}F NMR spectrum of 12-3 mud acid solution reacted with kaolinite at 75°F for 4 hours.

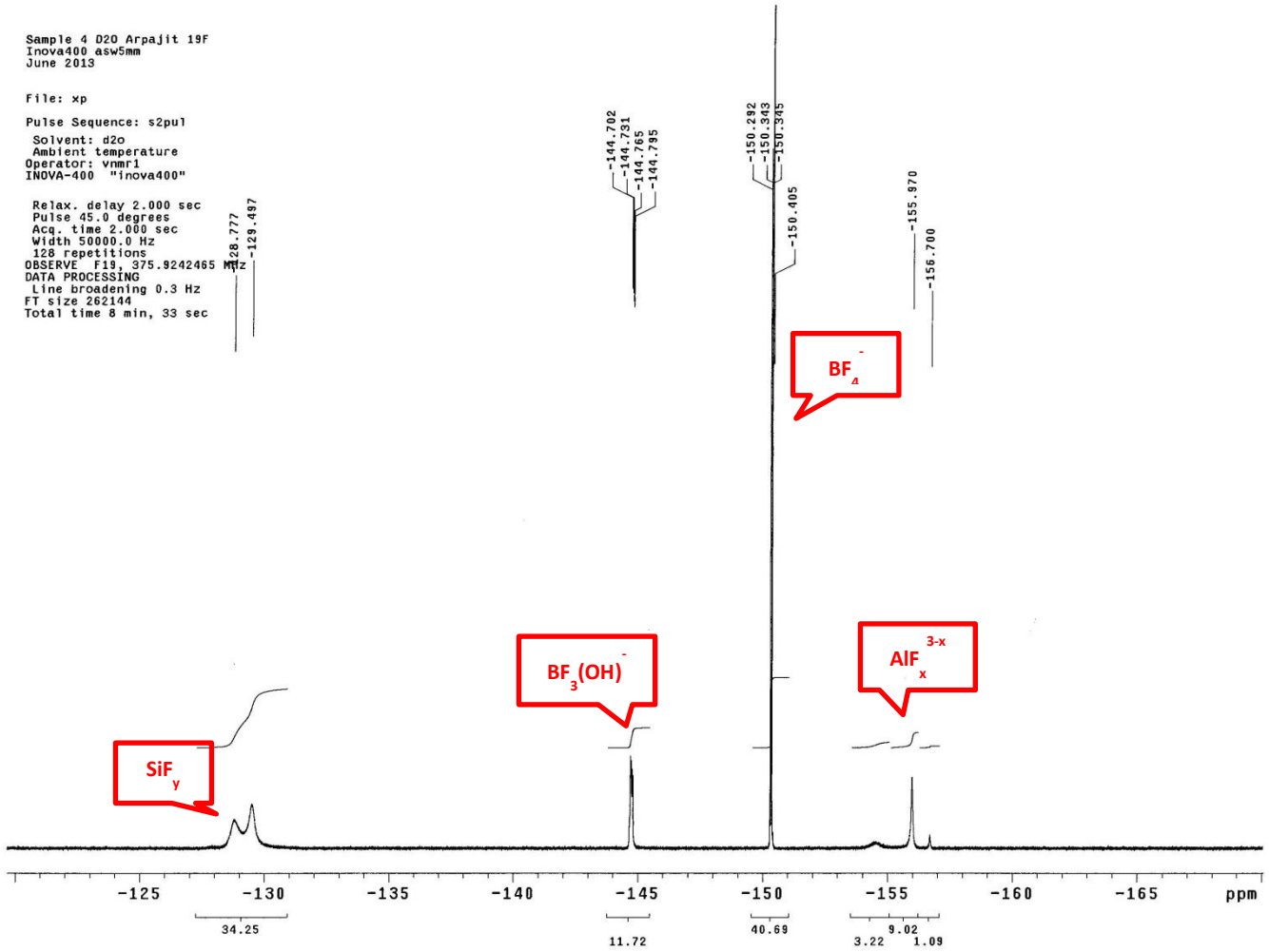

Figure 16: ^{19}F NMR spectrum of 3% HBF_4 solution reacted with kaolinite at 75°F for 4 hours.

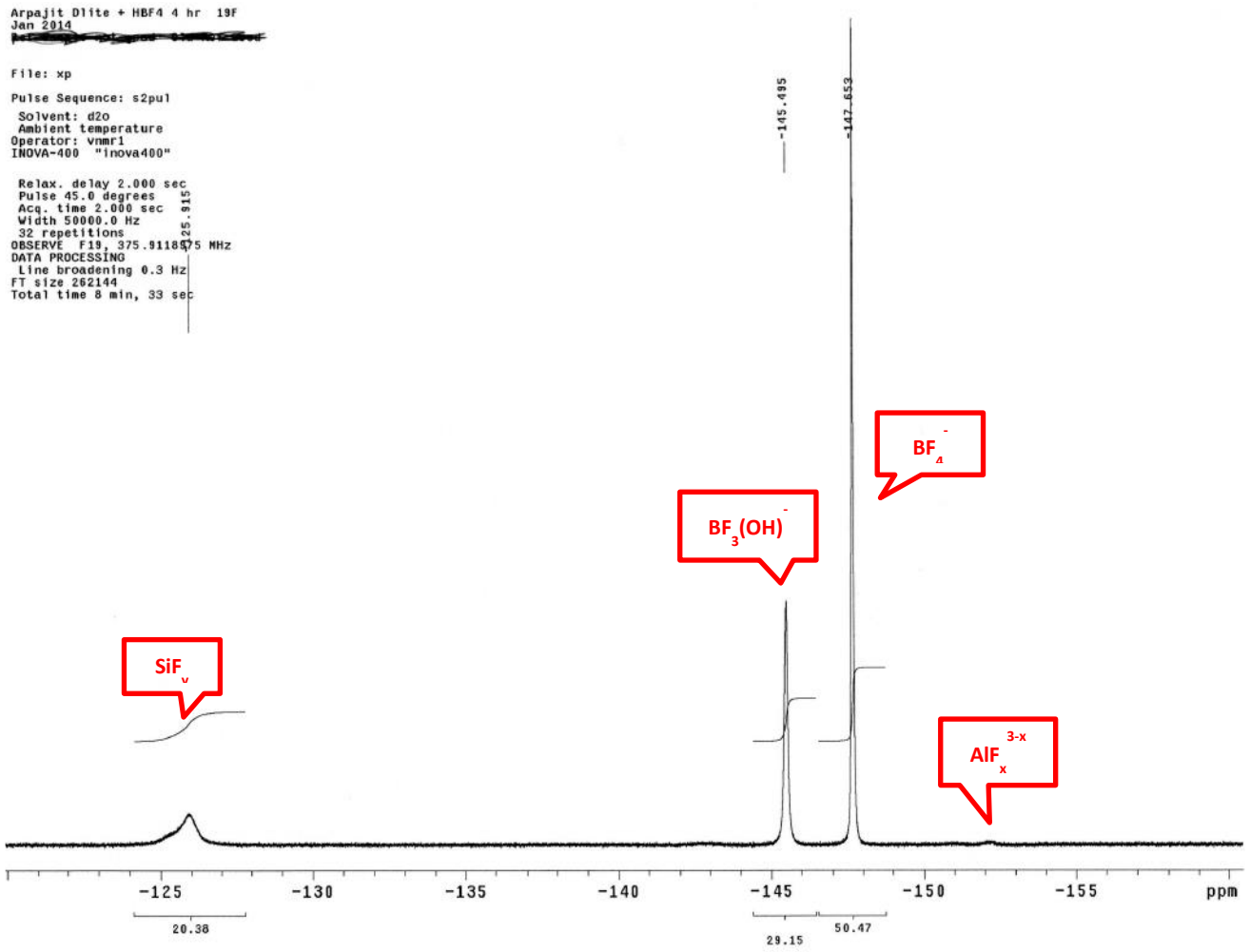

Figure 17: ^{19}F NMR spectrum of 3% HBF_4 solution reacted with illite at 75°F for 4 hours.

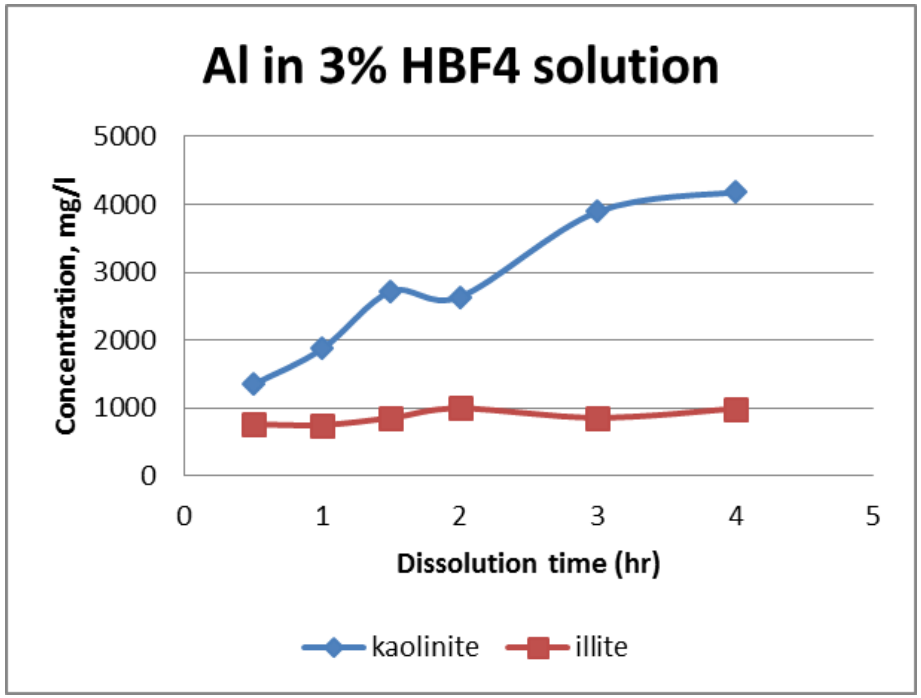

Figure 18: Al concentration available when reacting with different clay with 3% HBF_4 at 75°F.

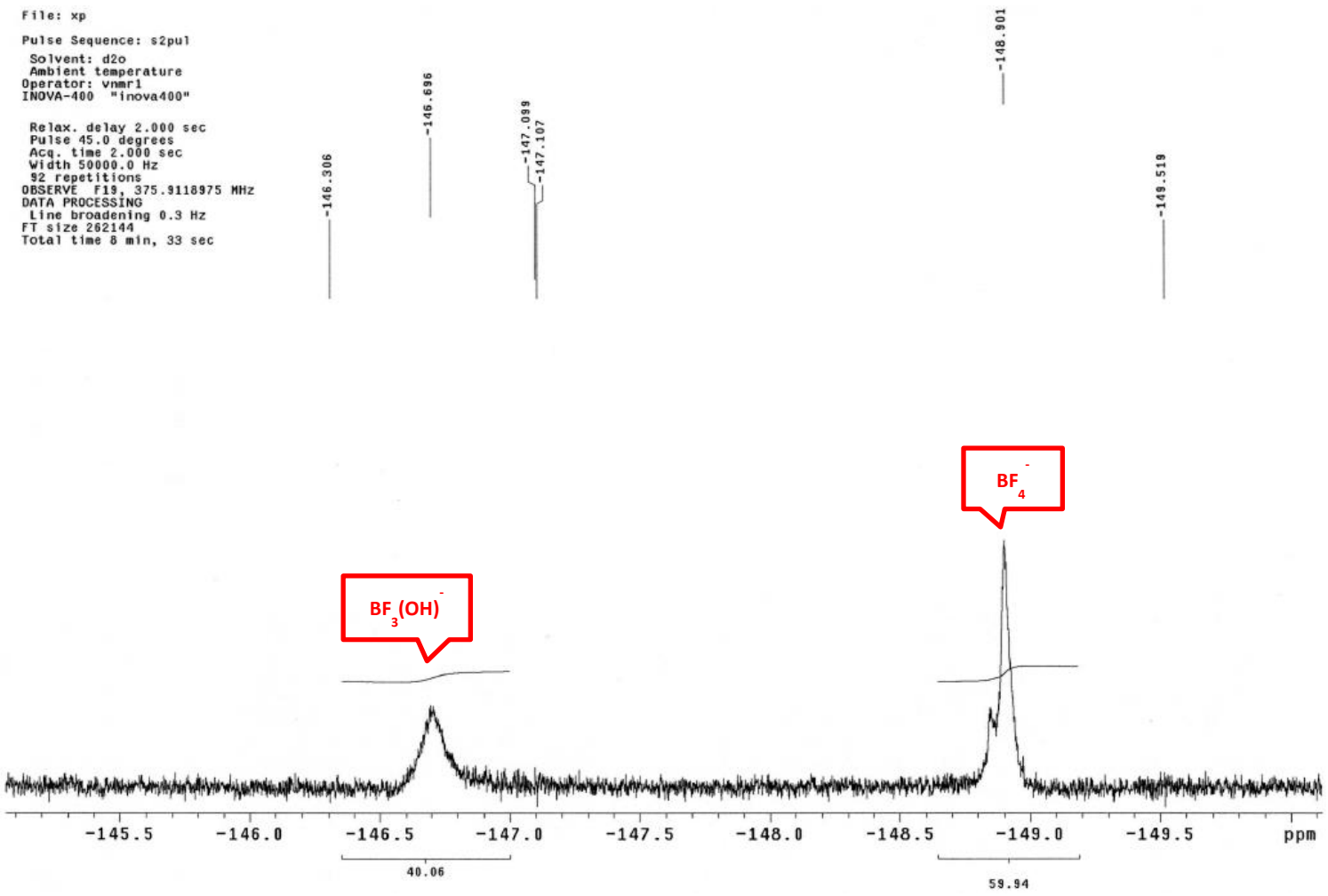

Figure 19: ^{19}F NMR spectrum of 3% HBF_4 solution reacted with bentonite at 75°F for 4 hours.

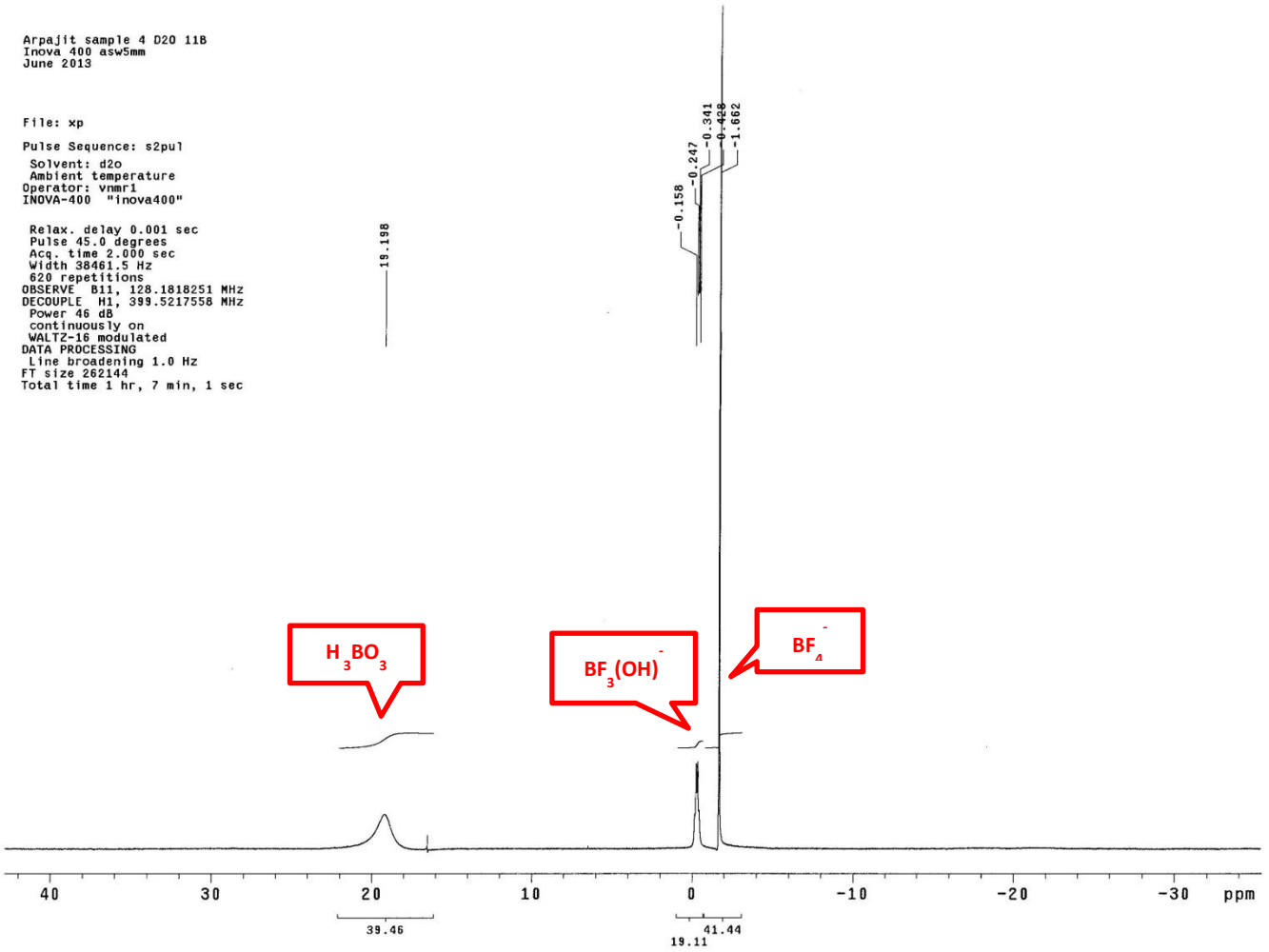

Figure 20: ^{11}B NMR spectrum of 3% HBF_4 solution reacted with kaolinite at 75°F for 4 hours.

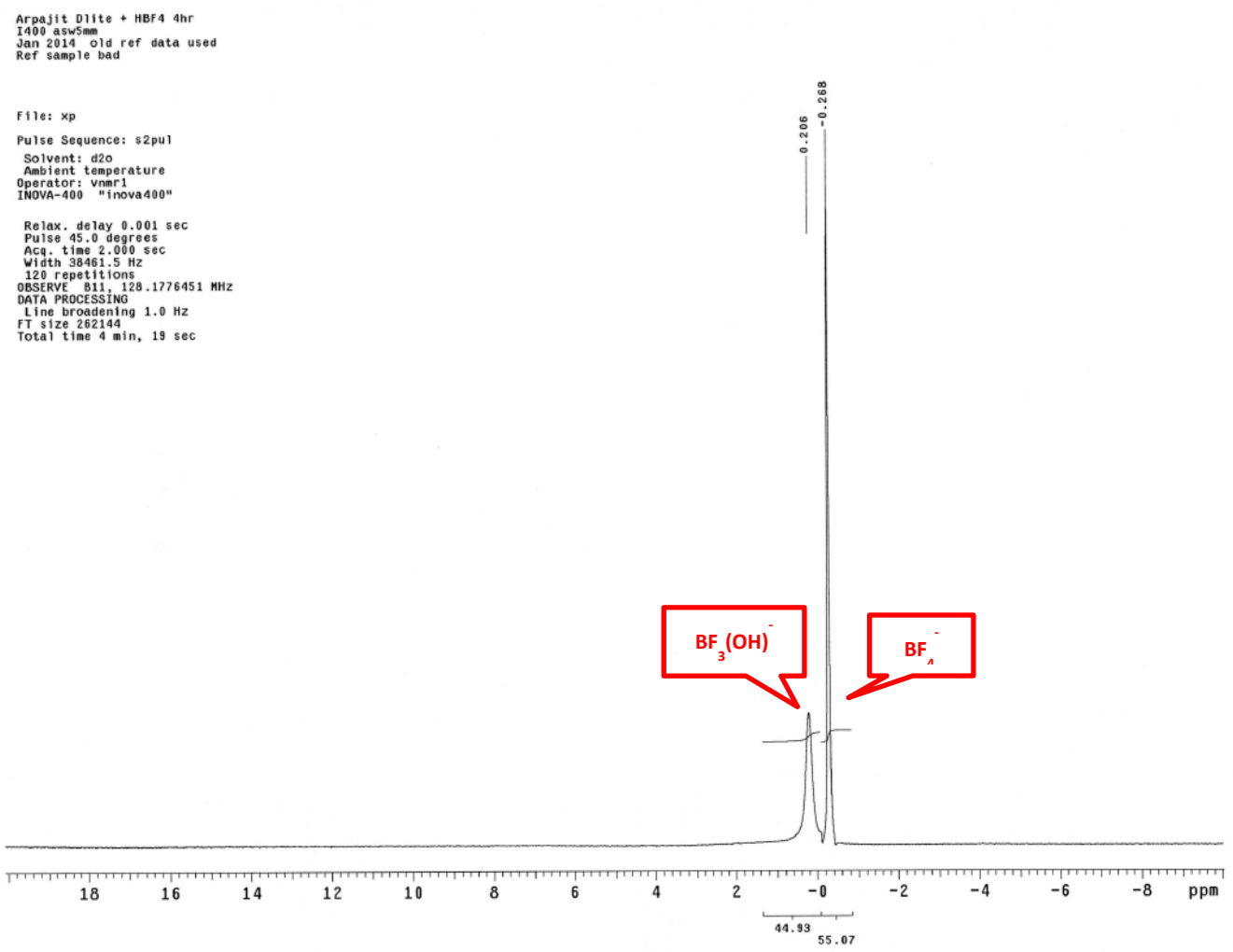

Figure 21: ^{11}B NMR spectrum of 3% HBF_4 solution reacted with illite at 75°F for 4 hours.

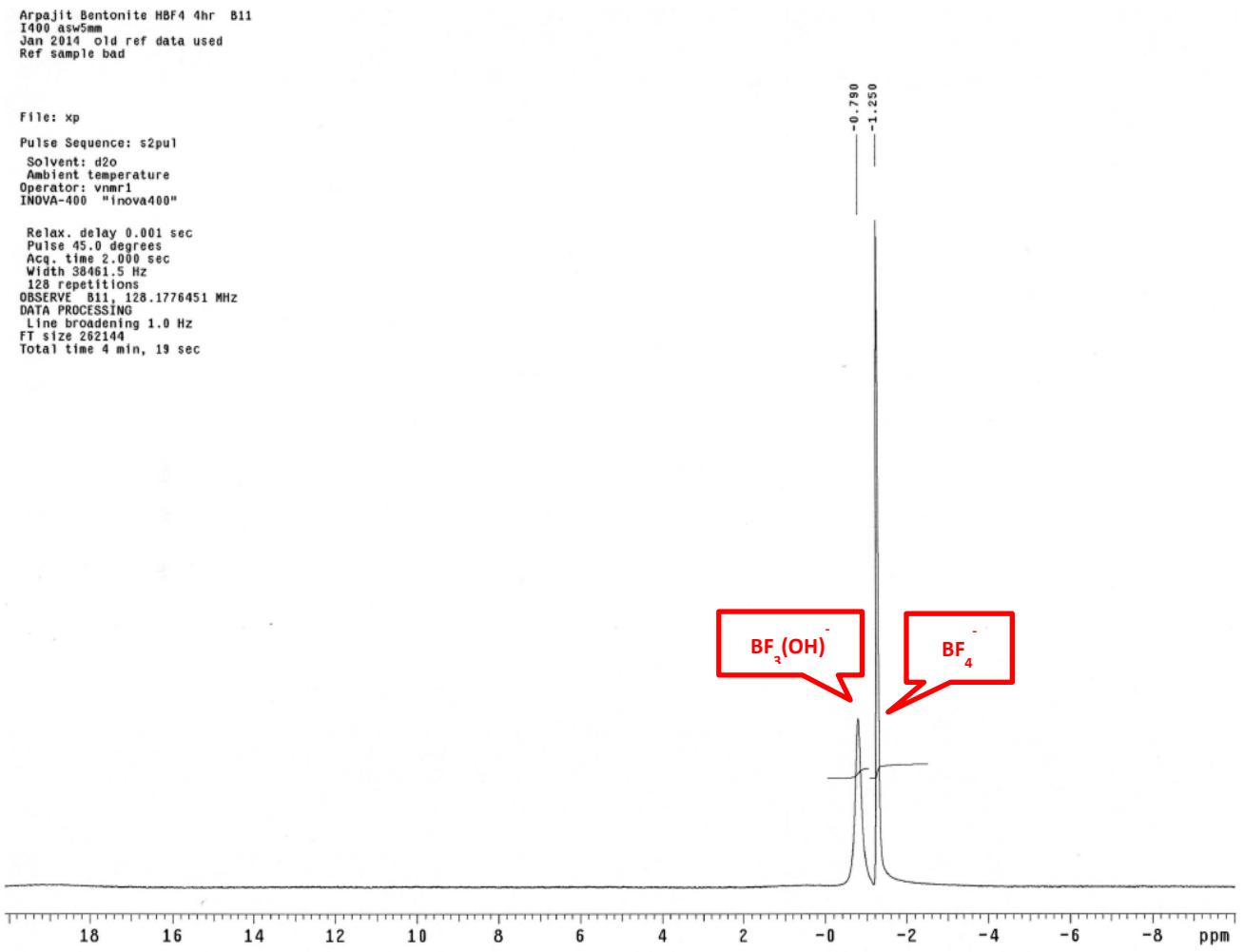

Figure 22: ^{11}B NMR spectrum of 3% HBF_4 solution reacted with bentonite at 75°F for 4 hours.

Clay Dissolution Test at 200°F

Comparing to 12-3 mud acid dissolvability at 200°F, the retardation effect of HBF_4 plunges down to about 2-3% as shown in Fig. 23.

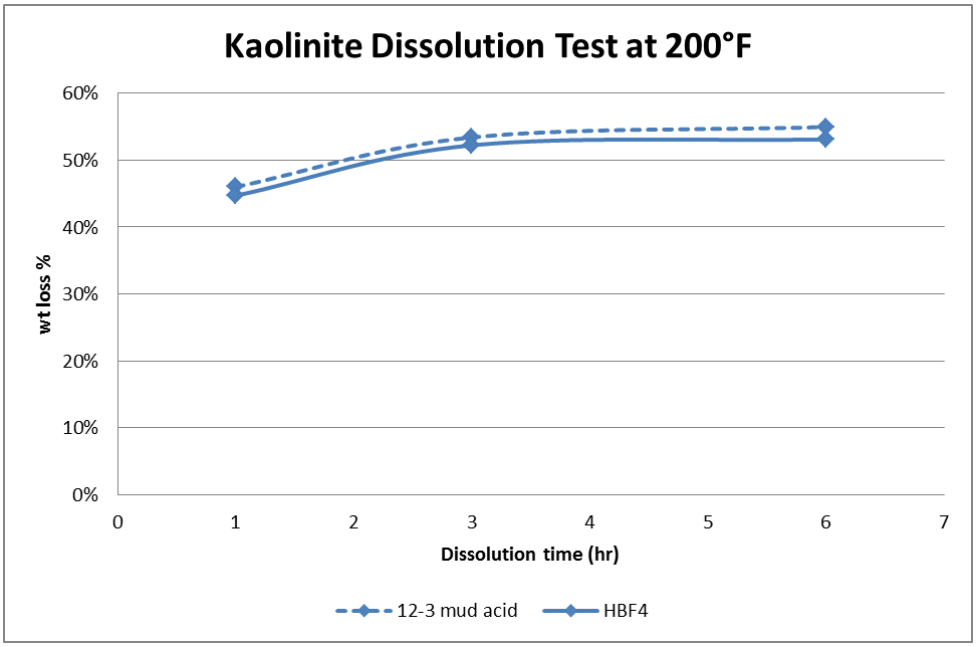

Figure 23: Kaolinite weight loss percent by 12-3 mud acid and 3% HBF_4 at 200°F.

Fig. 24 compares the reaction rate of HBF_4 on different clays at high temperature. The reaction rate has been raised for every clay tested at this temperature. It was observed that Bentonite lost its weight more than illite with HBF_4 at 200°F, and the opposite happened at 75°F.

The supernatant of HBF_4 with illite precipitated a white substance at all dissolution times (1,3,6 hours) as shown in Fig. 25, which later was analyzed with XRD

and identified as KBF_4. A match of KBF_4 from EVA database with XRD spectrum confirms its identity (Fig. 26).

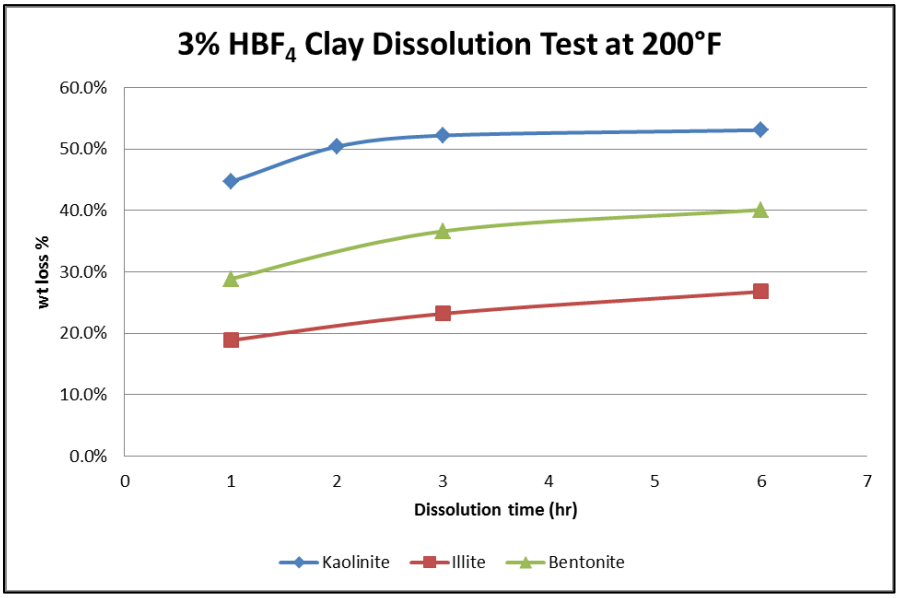

Figure 24: Clay weight loss percent by 3% HBF_4 at 200°F.

Figure 25: Precipitate from illite + HBF_4 dissolution at 200°F for 6 hours.

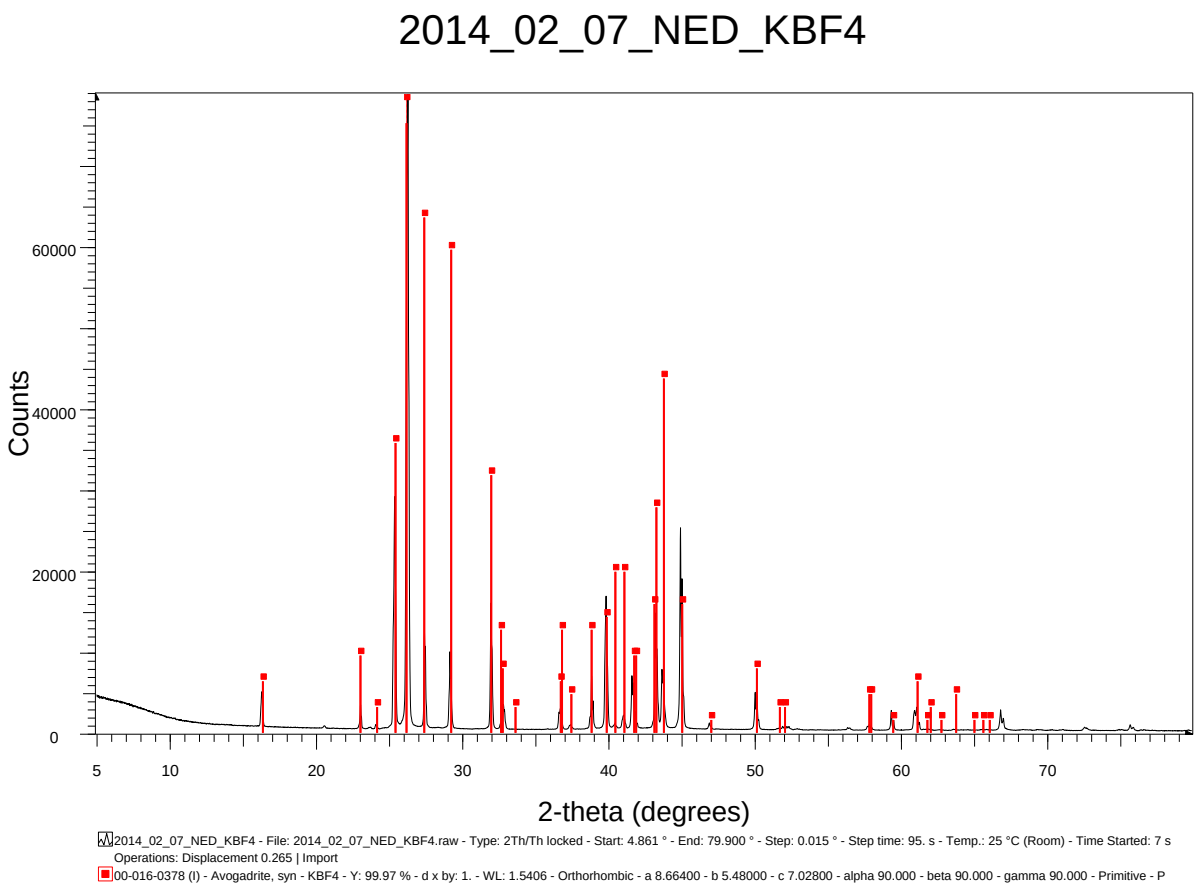

Figure 26: XRD spectrum matched with KBF_4 using EVA database.

The potassium concentration from 3% HBF_4 with illite at a higher temperature is lower. This can be accounted for due to the KBF_4 precipitation drawing K out of solution (Fig. 27).

Comparing key elements measured in the 3% HBF_4 supernatant of different clays (Fig. 28-30), a distinct falling trend of B in illite with acid solution is apparent. This is also resulted from KBF_4 precipitation.

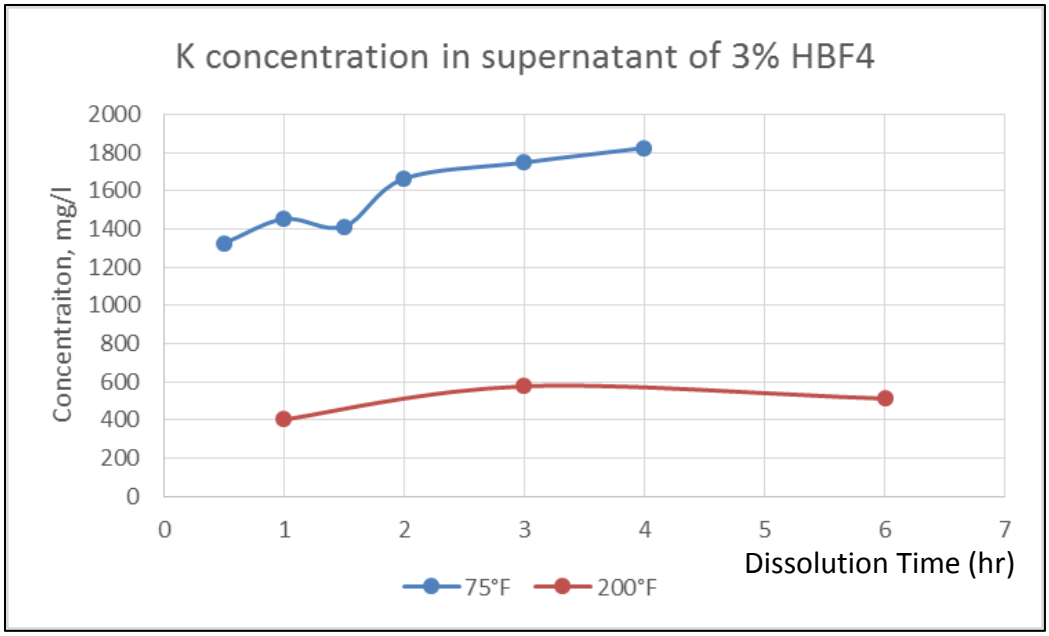

Figure 27: Potassium concentration leached from illite by 3% HBF_4 at different temperatures.

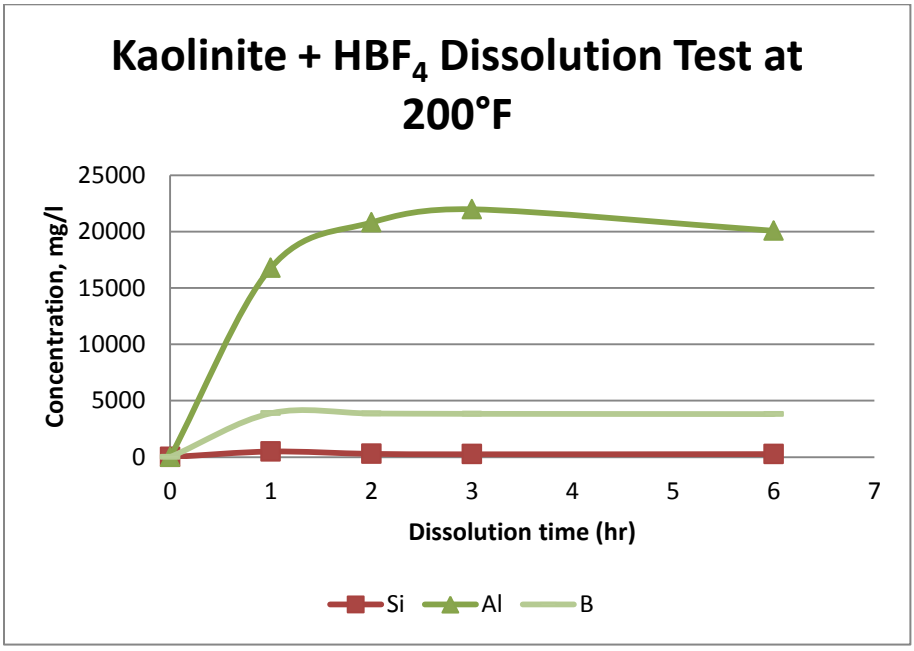

Figure 28: Key elements concentration in supernatant of kaolinite reacted with HBF_4 at 200°F.

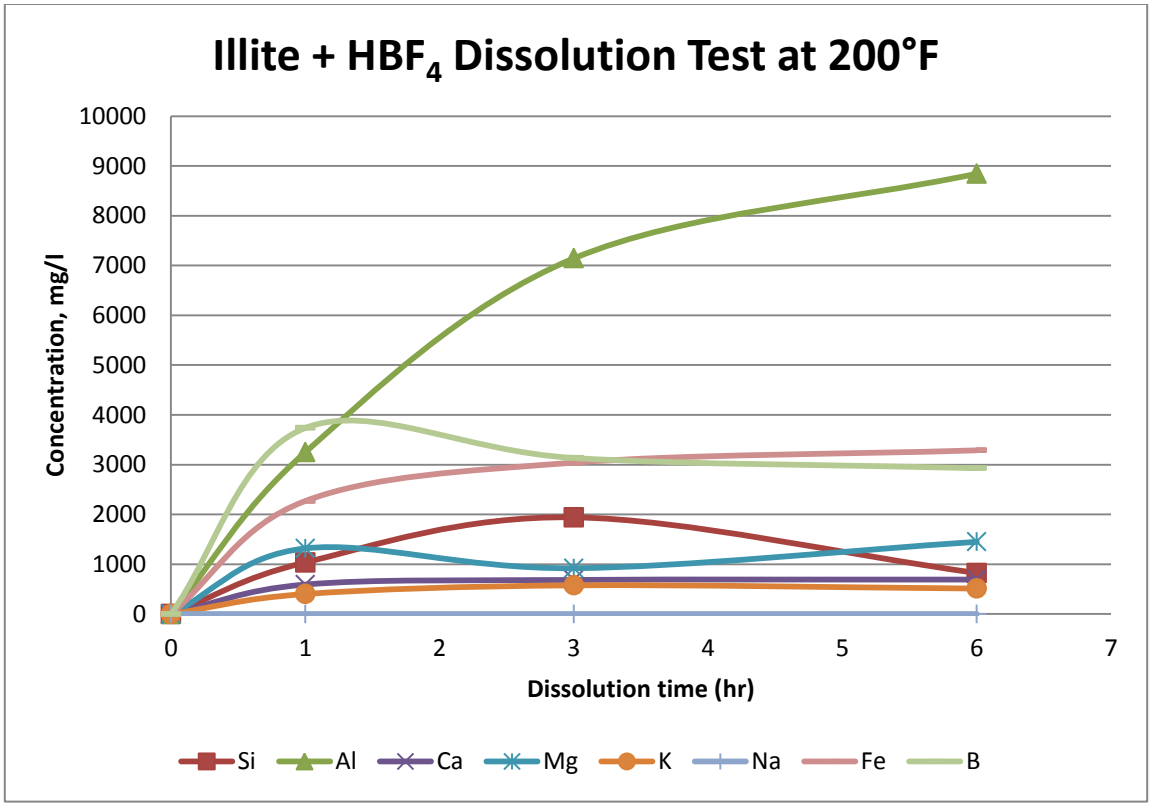

Figure 29: Key elements concentration in supernatant of illite reacted with HBF_4 at 200°F.

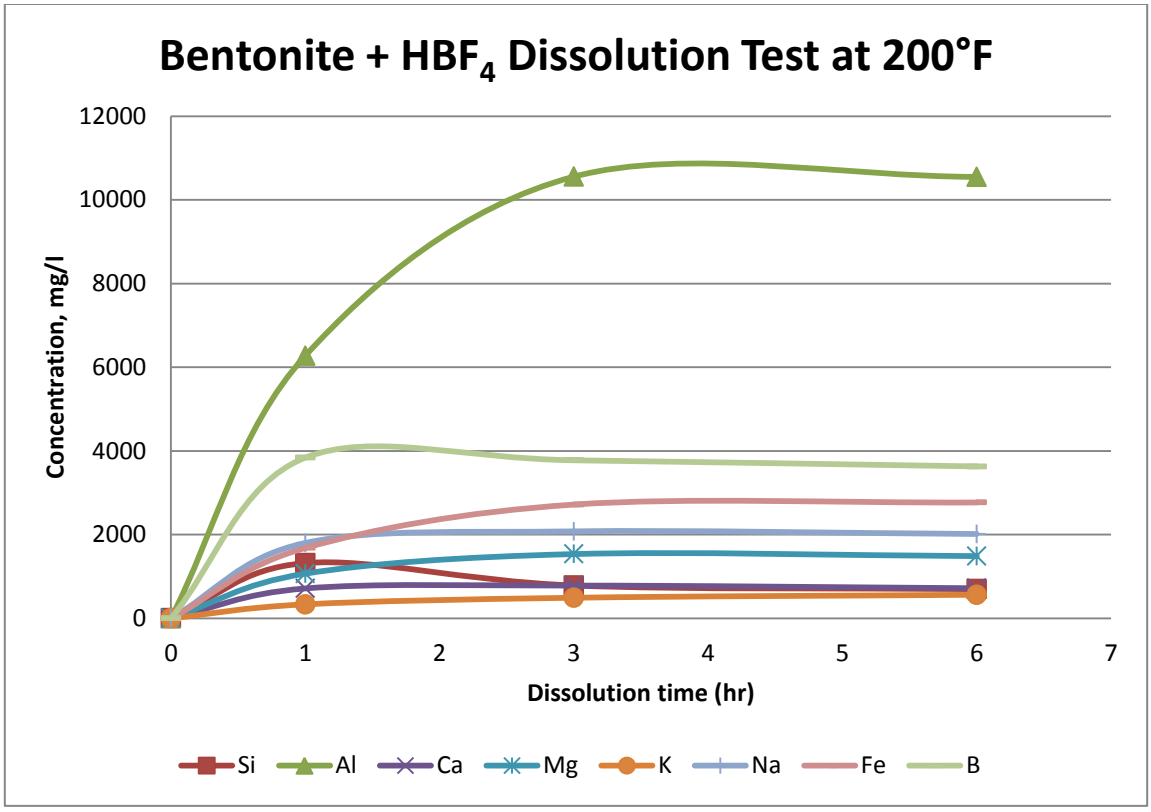

Figure 30: Key elements concentration in supernatant of bentonite reacted with HBF_4 at 200°F.

Fig. 31 contrasts the EDS spectrum of undissolved clays by 3% HBF_4 at 2 temperatures. At 200°F, HBF_4 leaches almost all Al from the clay structure (secondary reaction). Moreover, no SiF_y or $AlF_x^{(3-x)}$ precipitated in any clay, and no $NaBF_4$ precipitate in Bentonite.

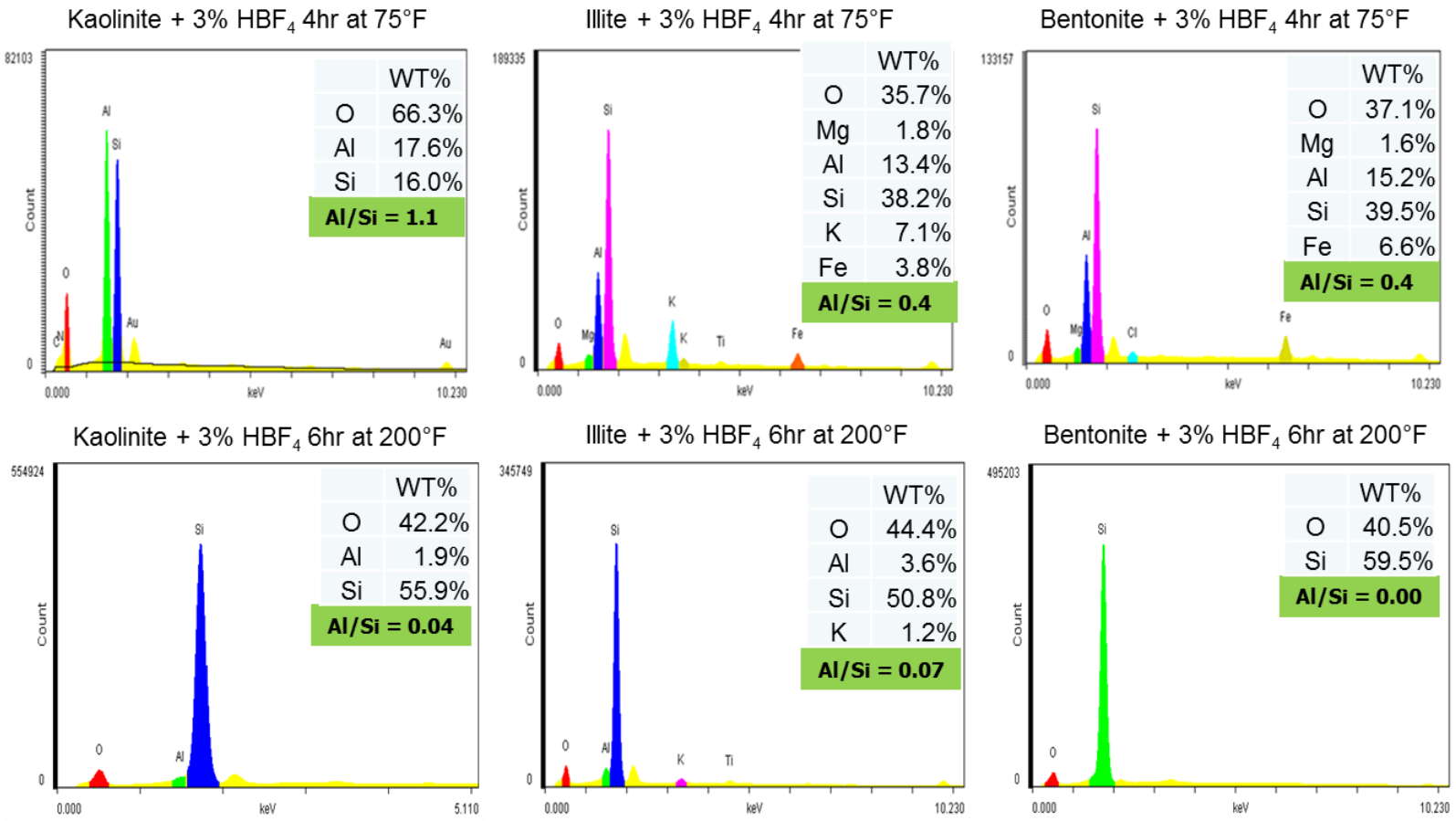

Figure 31: EDS spectra of 3% HBF_4 dissolved clays at 75°F for 4 hours (top row) vs 3% HBF_4 dissolved clays at 200°F for 6 hours.

Fig. 32-34 show comparisons of either Si or Al concentrations in 3% HBF_4 acid that had completed secondary reaction (200°F) with tests at 75°F. All show decreases of Si due to precipitation as amorphous silica and large increases in the Al leached.

An increase in the $AlF_x^{(3-x)}$ species noticed in Fig. 35 from Fig. 16 was due to a higher intensity of aluminum fluoride species compared to 75°F acid supernatant due to Al abundance in solution. A similar statement can also be implied on Fig. 36 and 37.

Fig. 38-40 yielded three similar species in every clay's supernatant (from left to right: H_3BO_3, BF_3OH^- and BF_4^-). It can then be concluded that a significant reaction is going on at this temperature for each clay with 3% HBF_4.

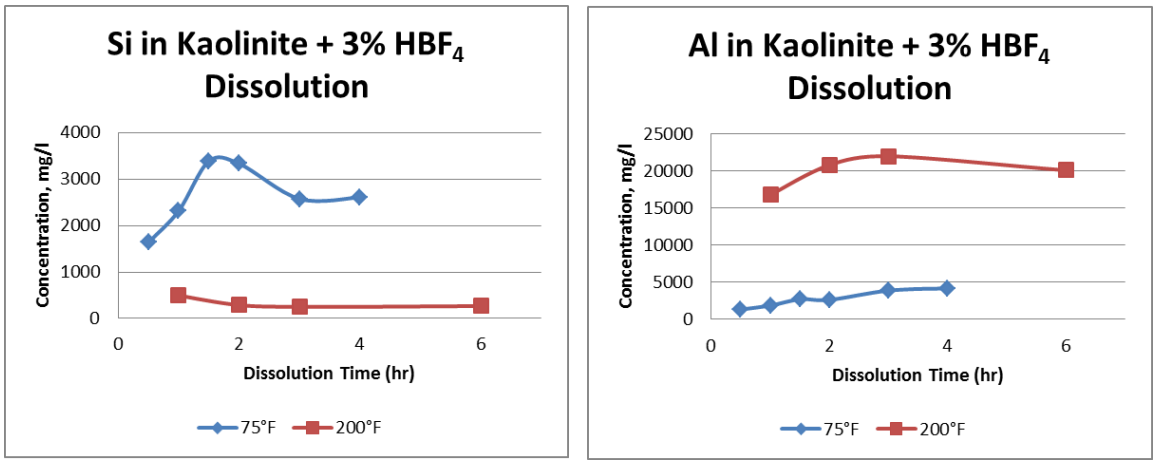

Figure 32: Effect of temperature on Si and Al concentrations in 3% HBF_4 supernatant with kaolinite.

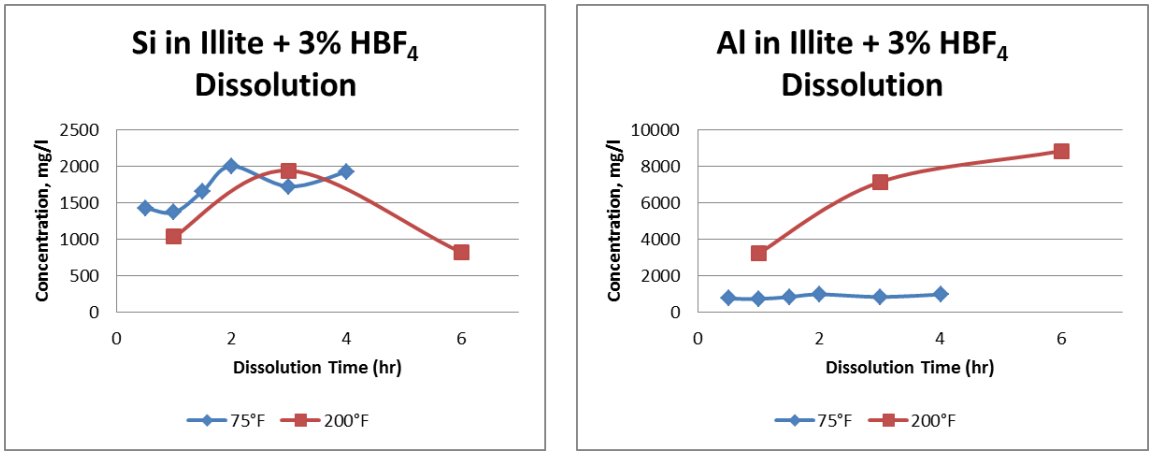

Figure 33: Effect of temperature on Si and Al concentrations in 3% HBF_4 supernatant with illite.

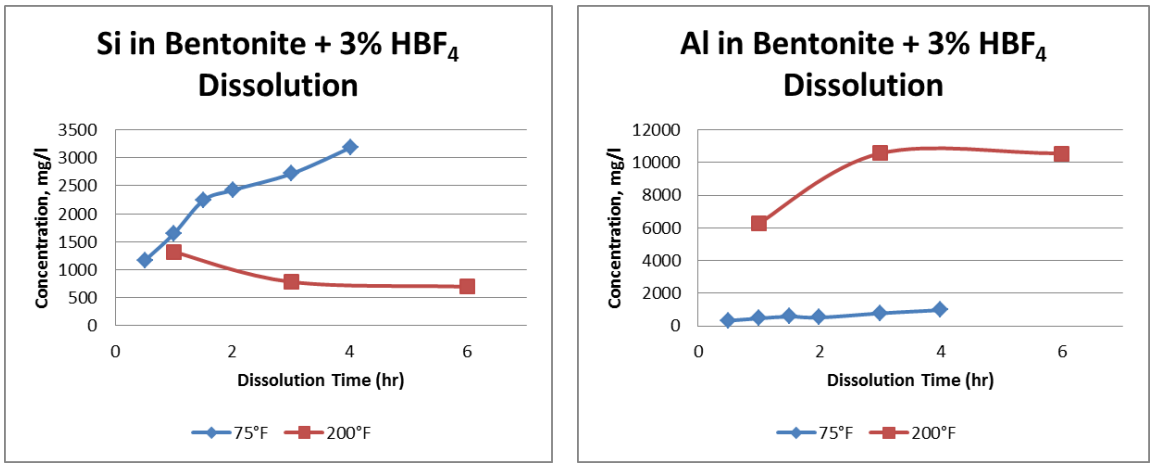

Figure 34: Effect of temperature on Si and Al concentrations in 3% HBF_4 supernatant with bentonite.

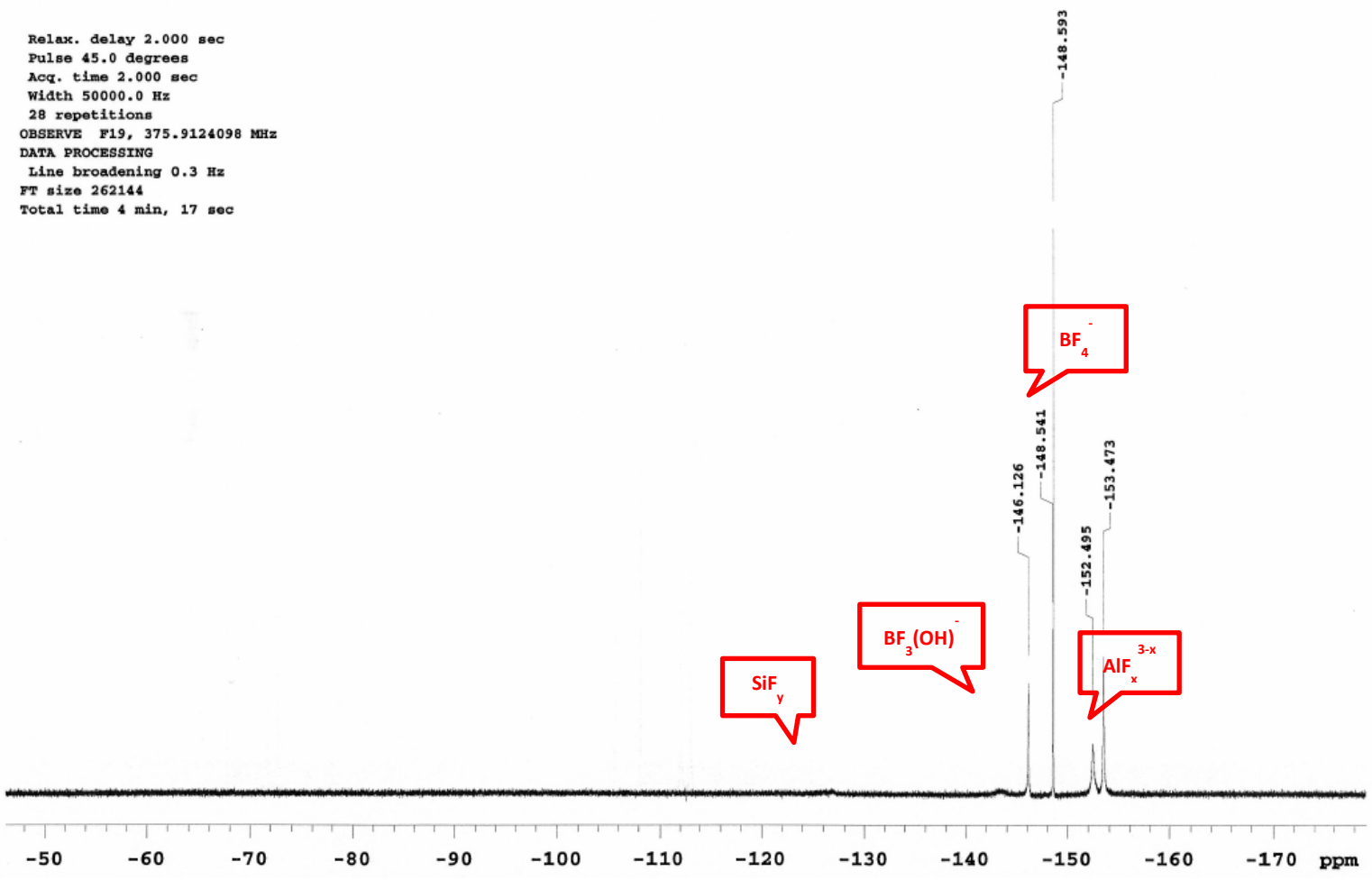

Figure 35: ^{19}F NMR spectrum of 3% HBF_4 solution reacted with kaolinite at 200°F for 6 hours.

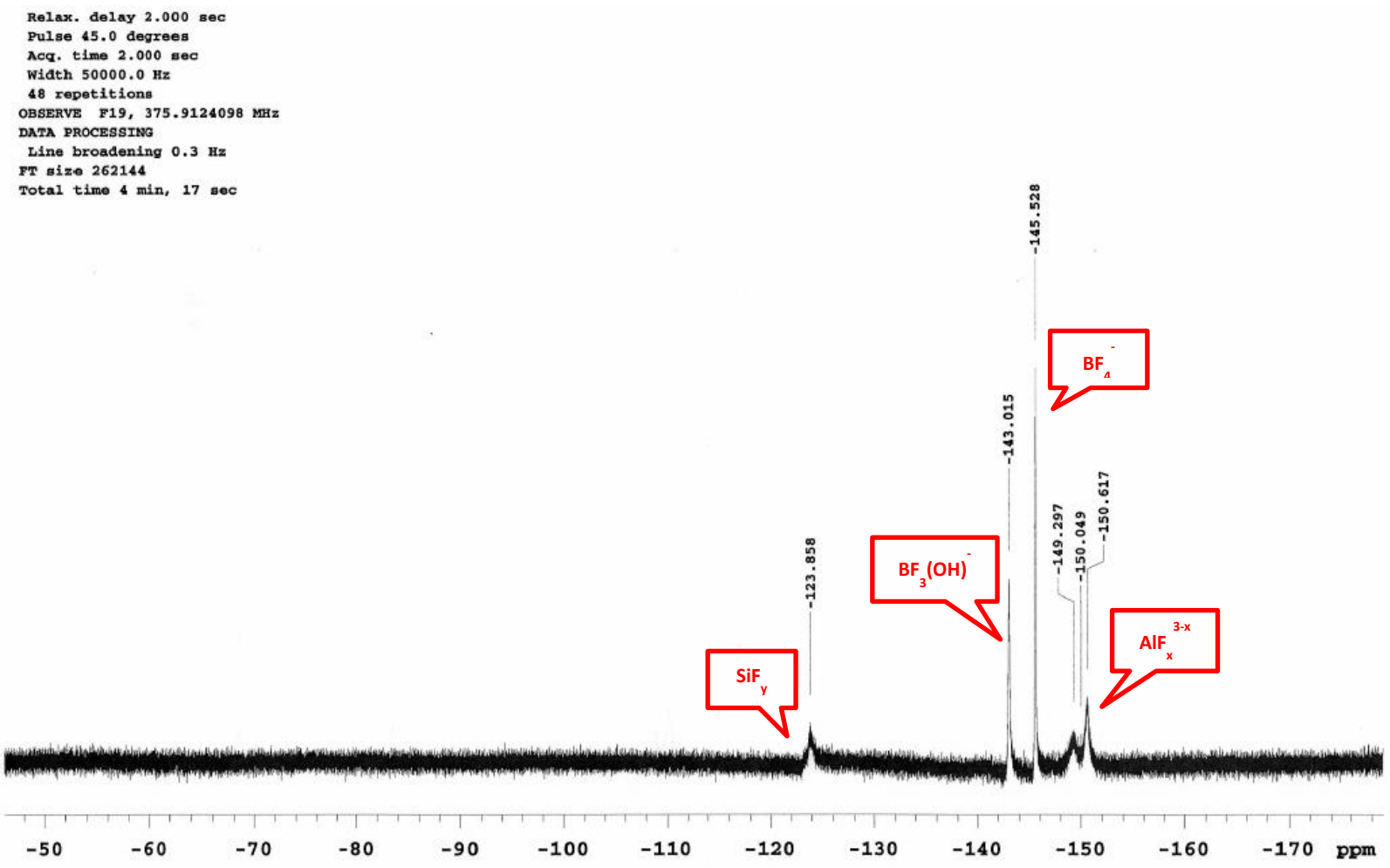

Figure 36: ^{19}F NMR spectrum of 3% HBF_4 solution reacted with illite at 200°F for 6 hours.

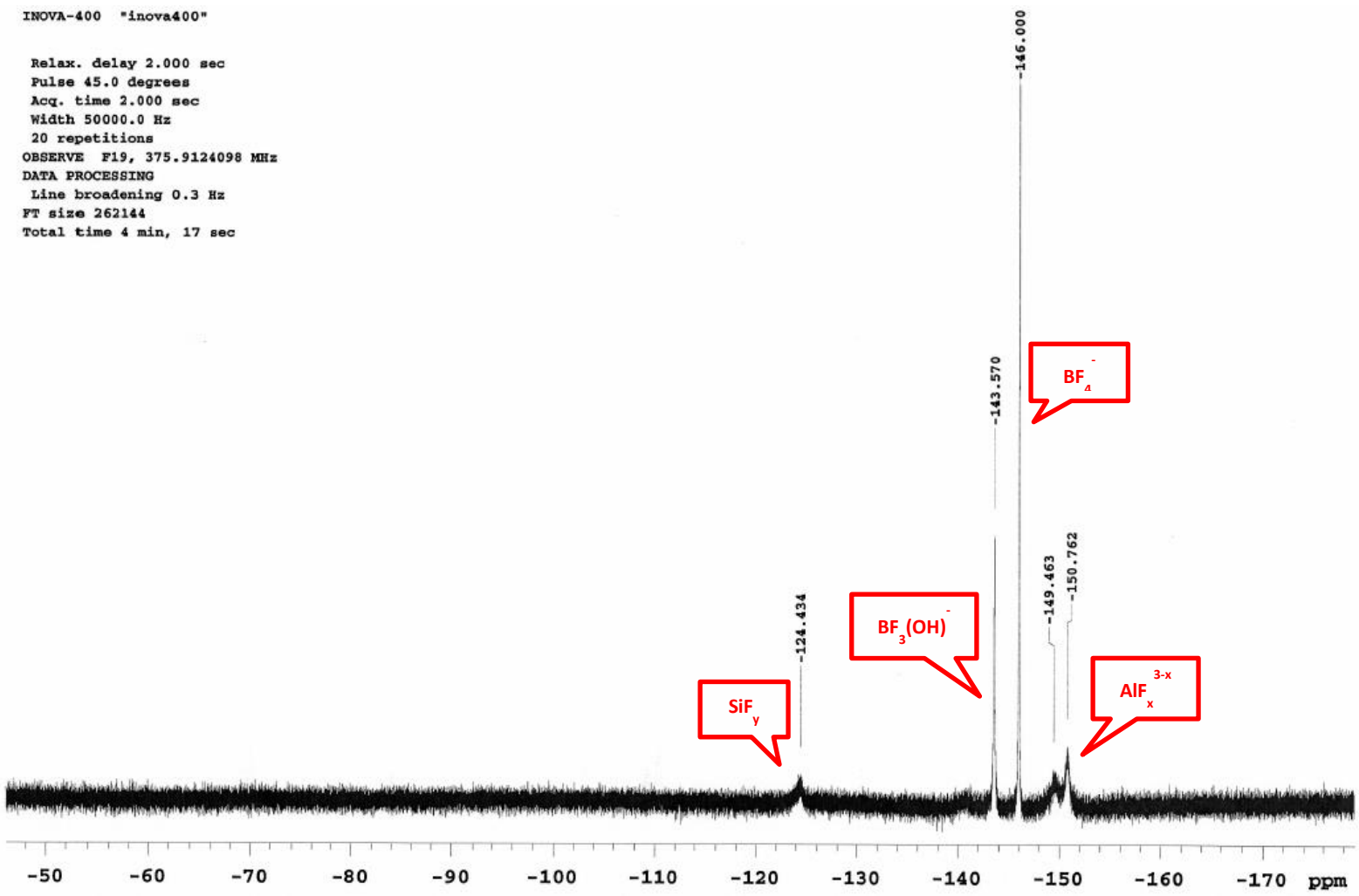

Figure 37: ^{19}F NMR spectrum of 3% HBF_4 solution reacted with bentonite at 200°F for 6 hours.

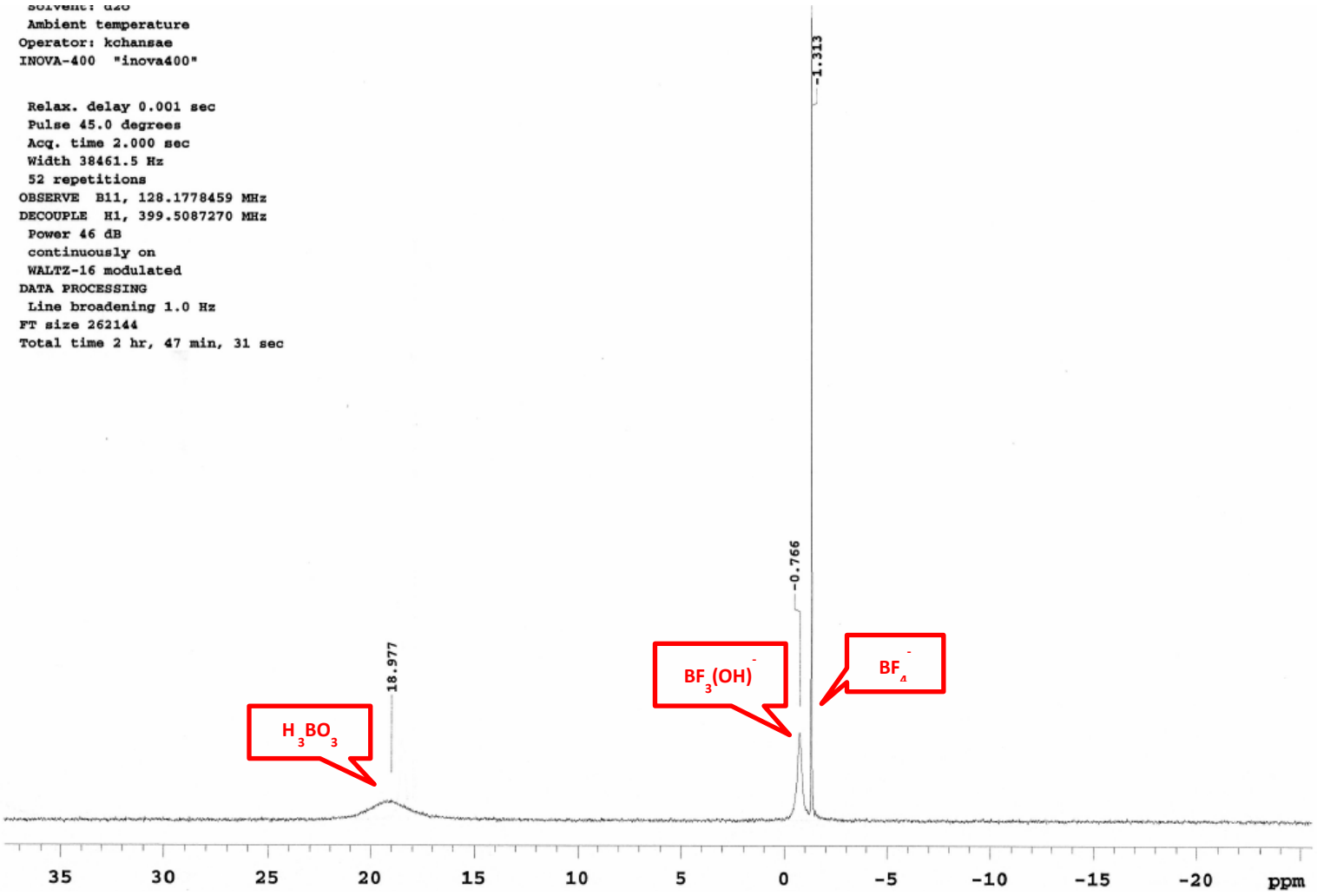

Figure 38: ^{11}B NMR spectrum of 3% HBF_4 solution reacted with kaolinite at 200°F for 6 hours.

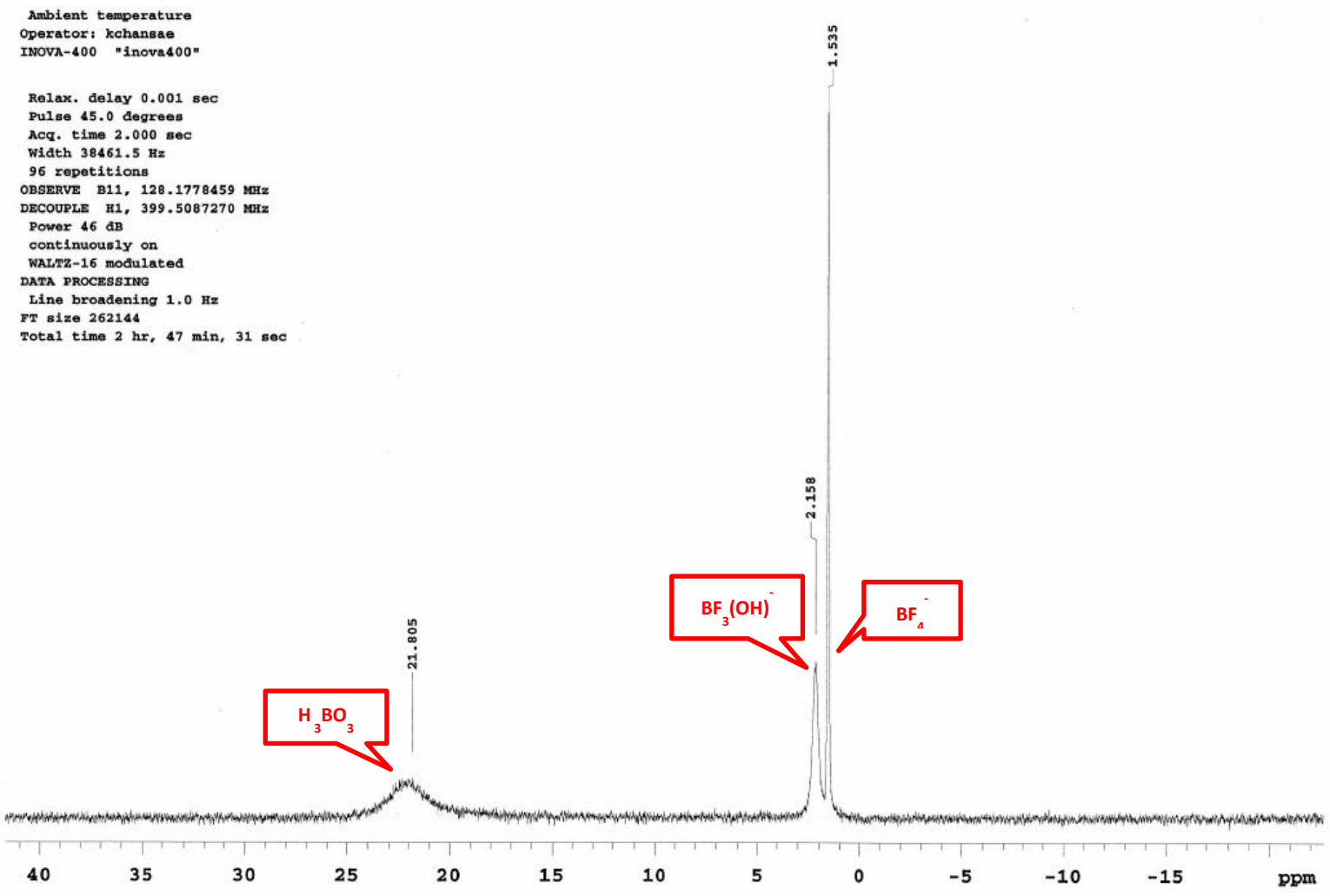

Figure 39: ^{11}B NMR spectrum of 3% HBF_4 solution reacted with illite at 200°F for 6 hours.

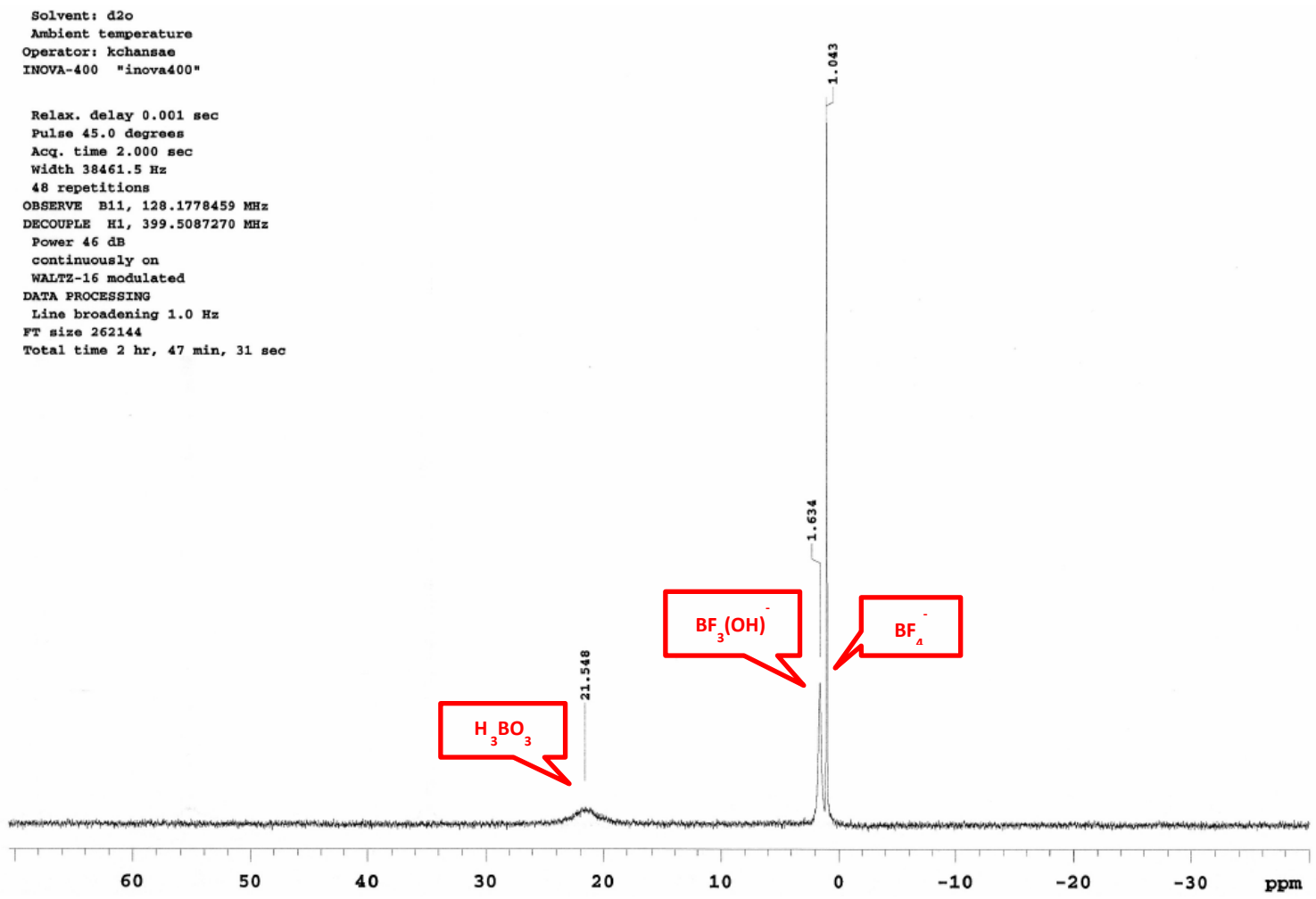

Figure 40: ^{11}B NMR spectrum of 3% HBF_4 solution reacted with bentonite at 200°F for 6 hours.

Berea Sandstone Coreflood at 200°F

Corefloods in Berea sandstone with 3% and 8% mud acid resulted in a permeability reduction of 34% (Fig. 41) and 22% (Fig. 46) respectively. This is suspected to be caused by amorphous silica precipitation blocking pore throats. The falling of Si concentration in the effluent samples after 1 hour acid shut-in in both corefloods in Fig. 42 and 47 can support this thinking. All other key elements concentration are shown in Fig. 44-45 and Fig. 49-50.

A 5 wt% HCl preflush of 5 PV has proven to be sufficient judging from the low level of Ca even before that stage is done (Fig. 43,48 and 53). Fig. 52 illustrates how the Si trend should look if the core was stimulated with 12-3 mud acid and HF was not shut-in, which would induce less precipitation and would not damage the core (Fig. 51). All other key elements concentration from mud acid coreflood are shown in Fig. 54-55.

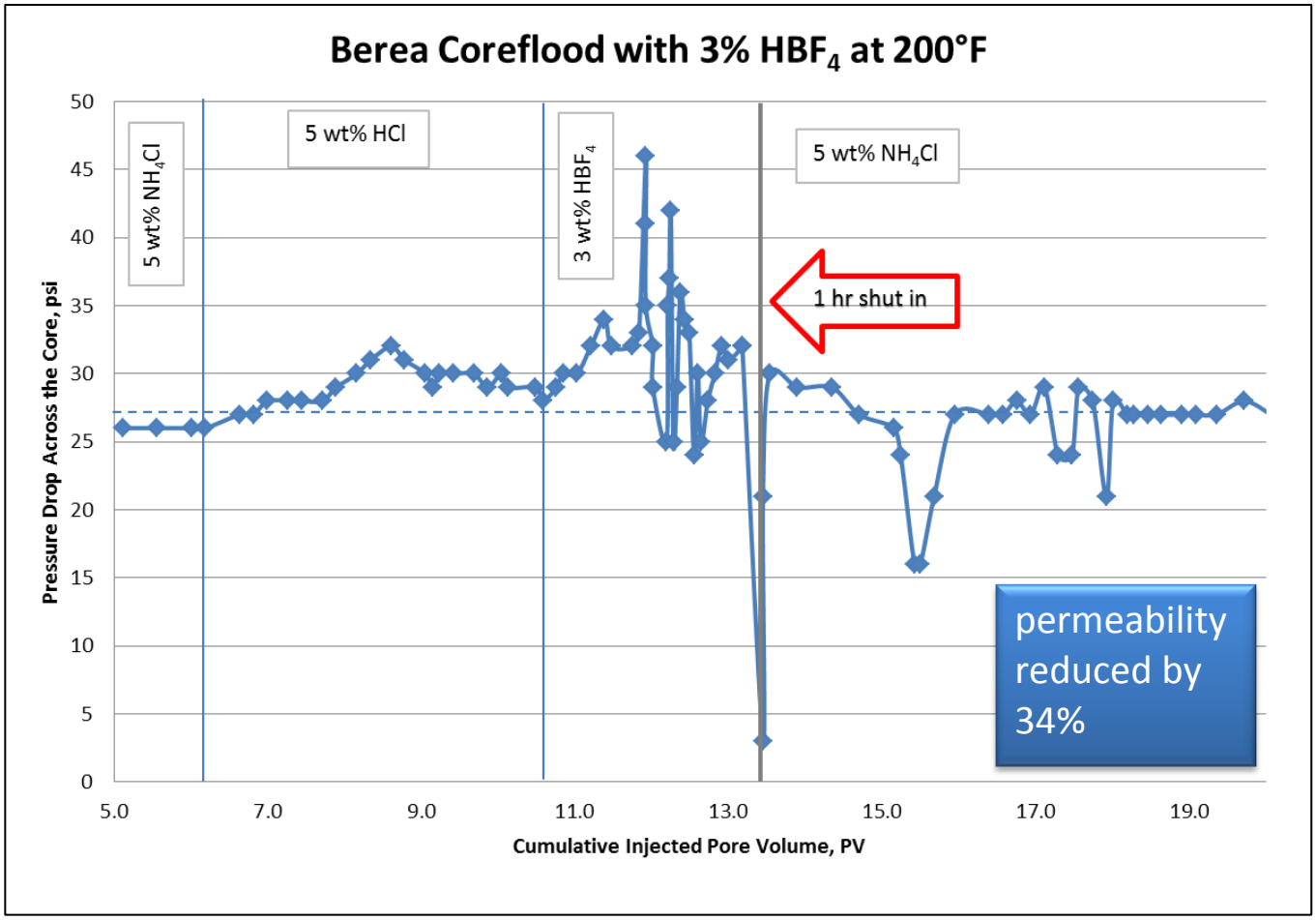

Figure 41: Pressure drop across the core during injection in Berea sandstone with 3% HBF_4 main acid at 200°F.

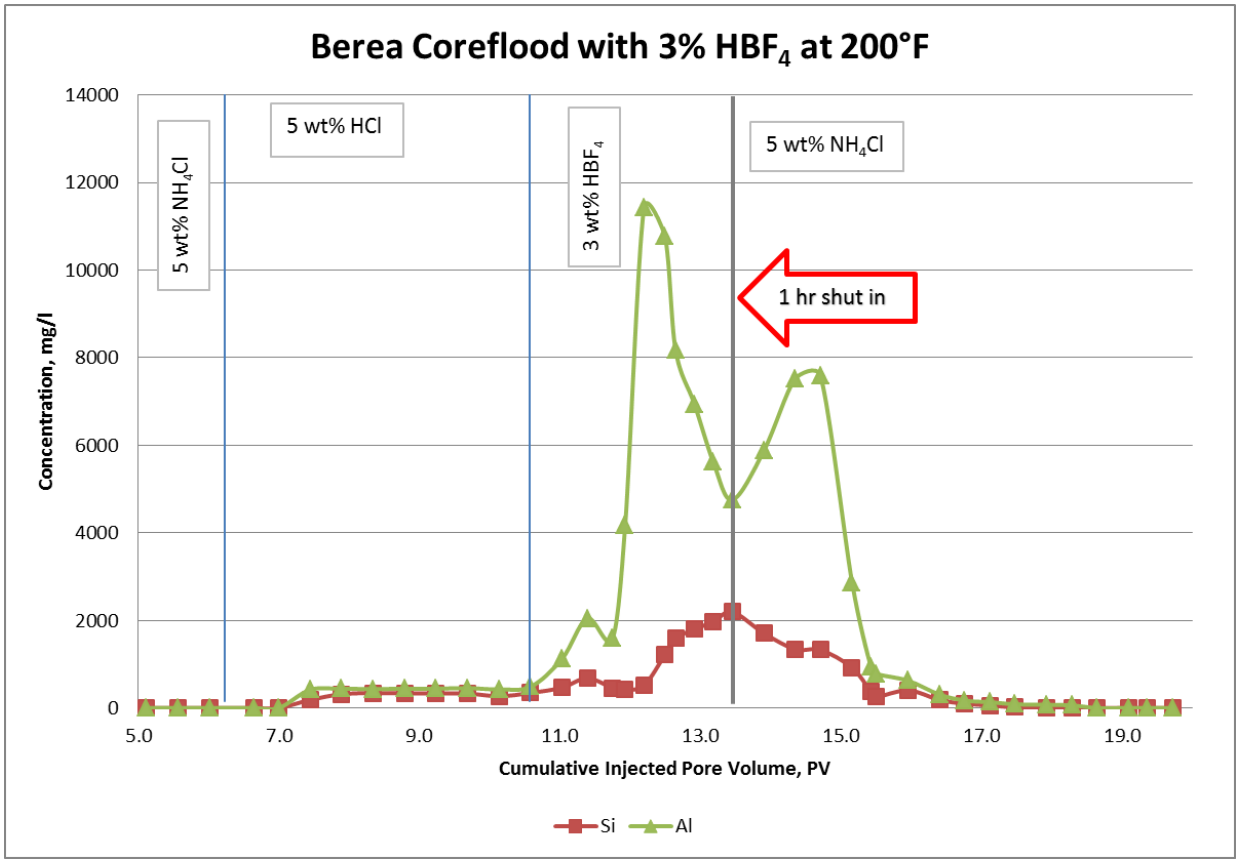

Figure 42: Si and Al concentrations in Berea coreflood effluent samples at 200°F with 3% HBF_4 main acid.

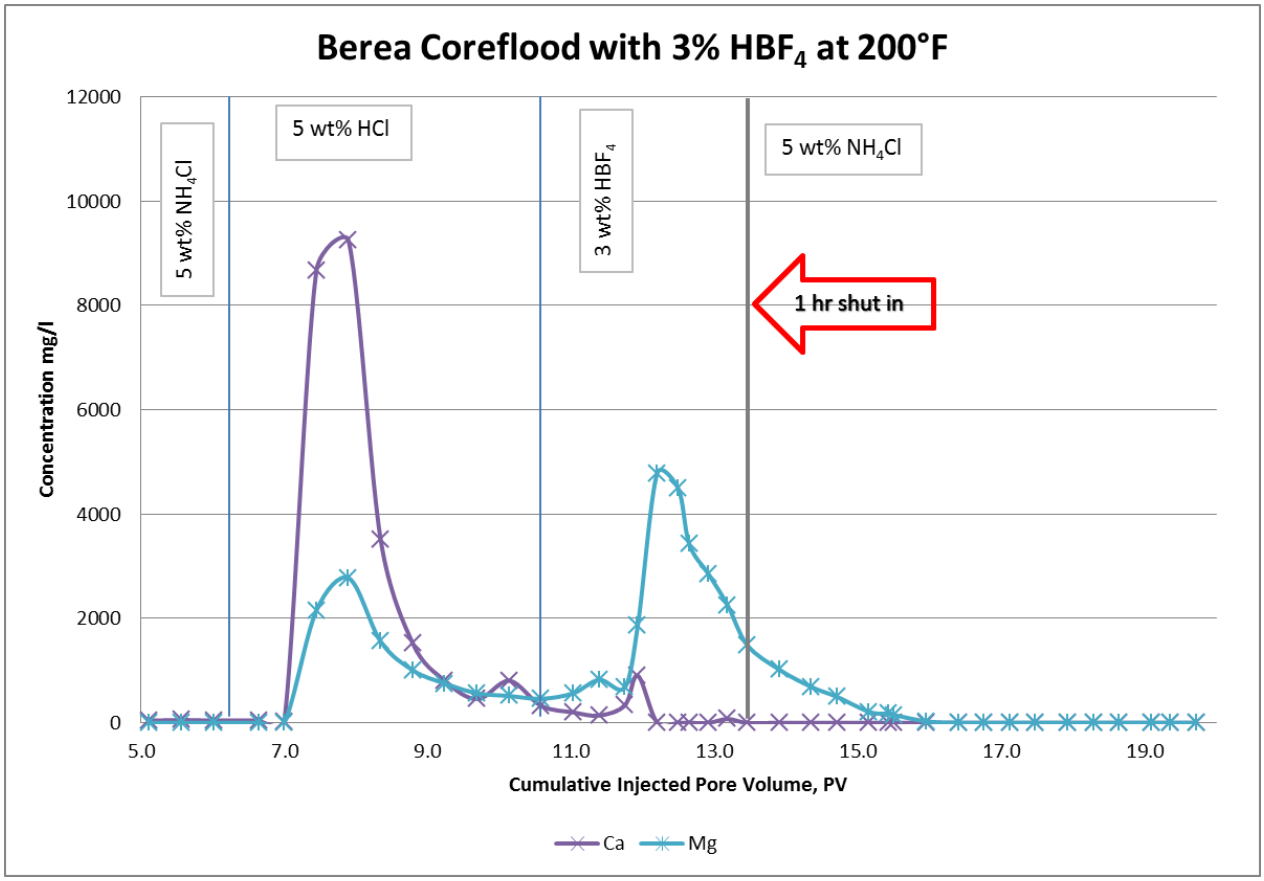

Figure 43: Ca and Mg concentrations in Berea coreflood effluent samples at 200°F with 3% HBF_4 main acid.

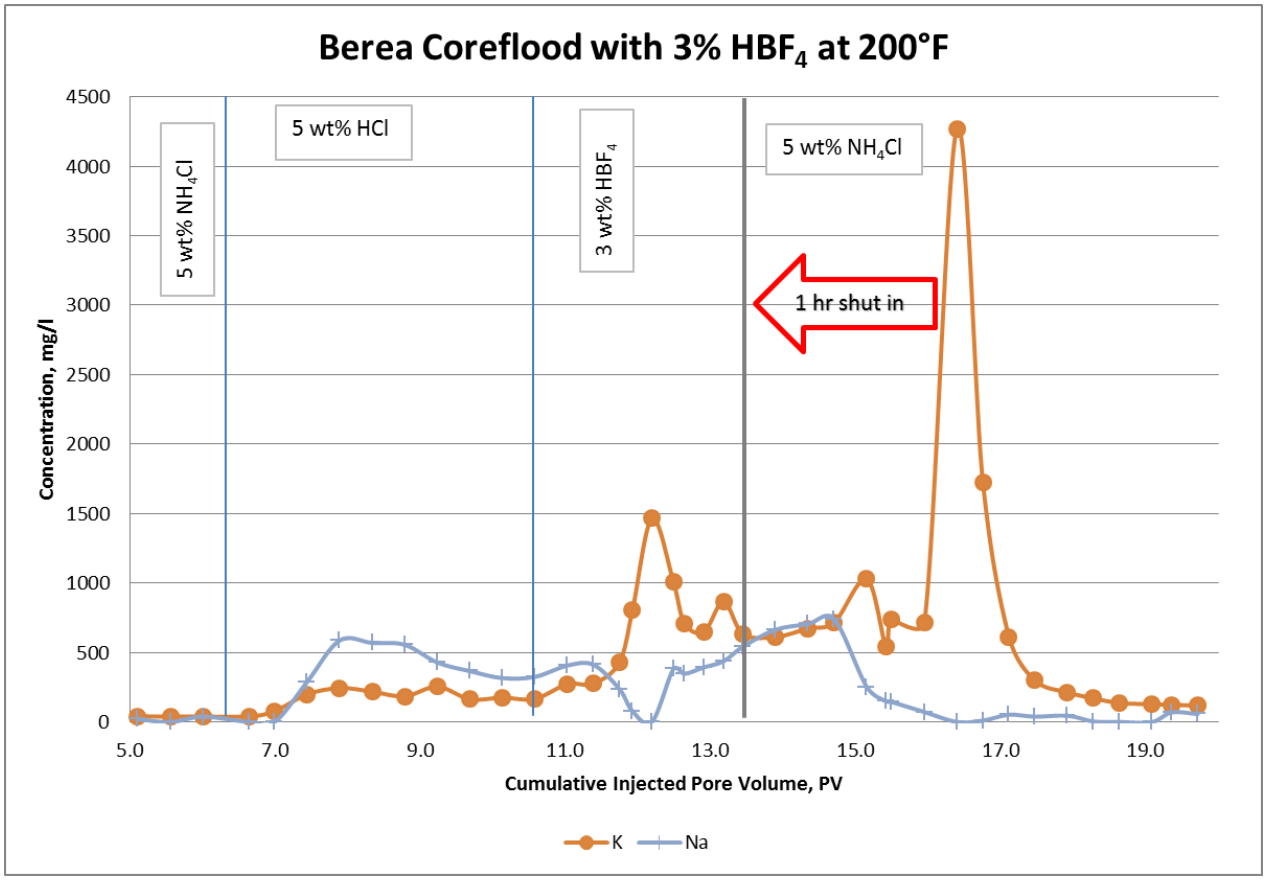

Figure 44: K and Na concentrations in Berea coreflood effluent samples at 200°F with 3% HBF_4 main acid.

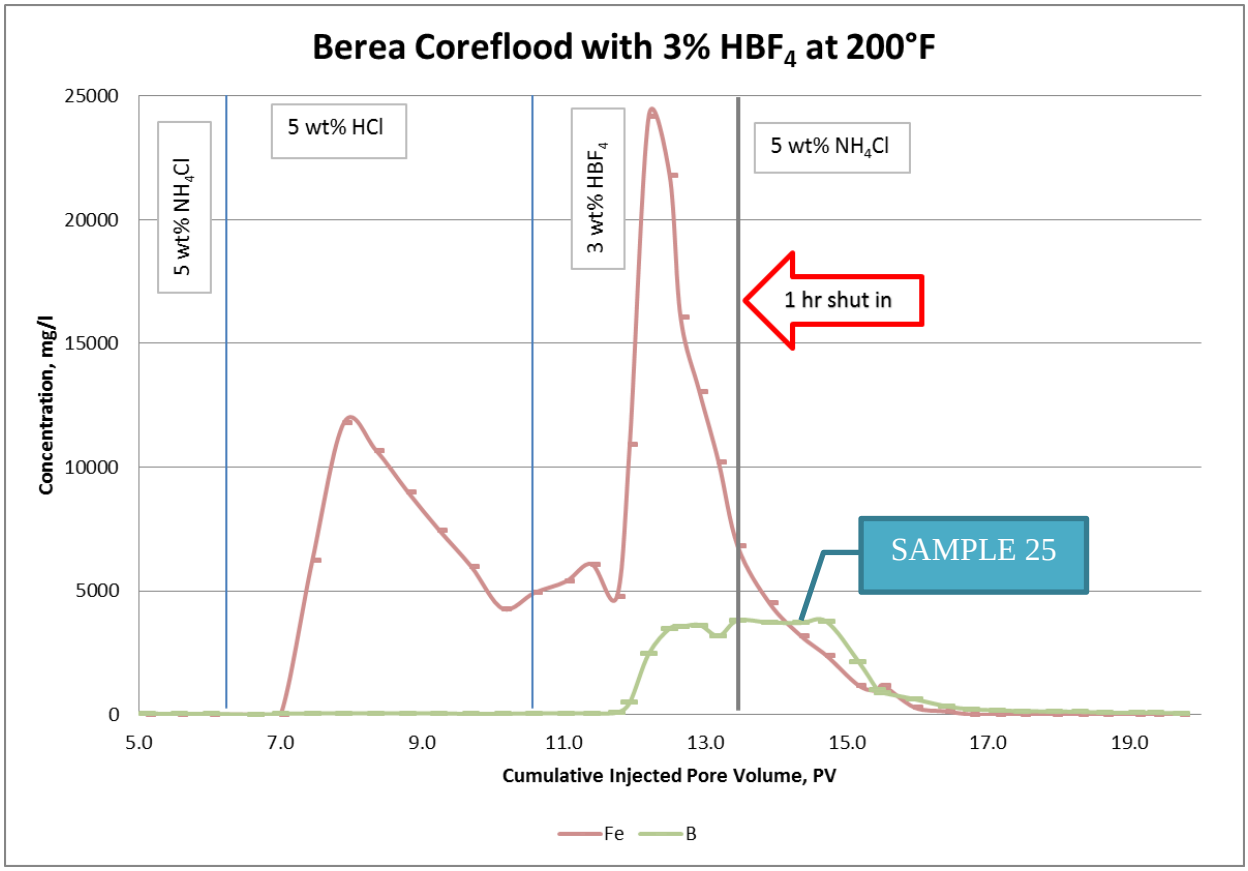

Figure 45: Fe and B concentrations in Berea coreflood effluent samples at 200°F with 3% HBF_4 main acid.

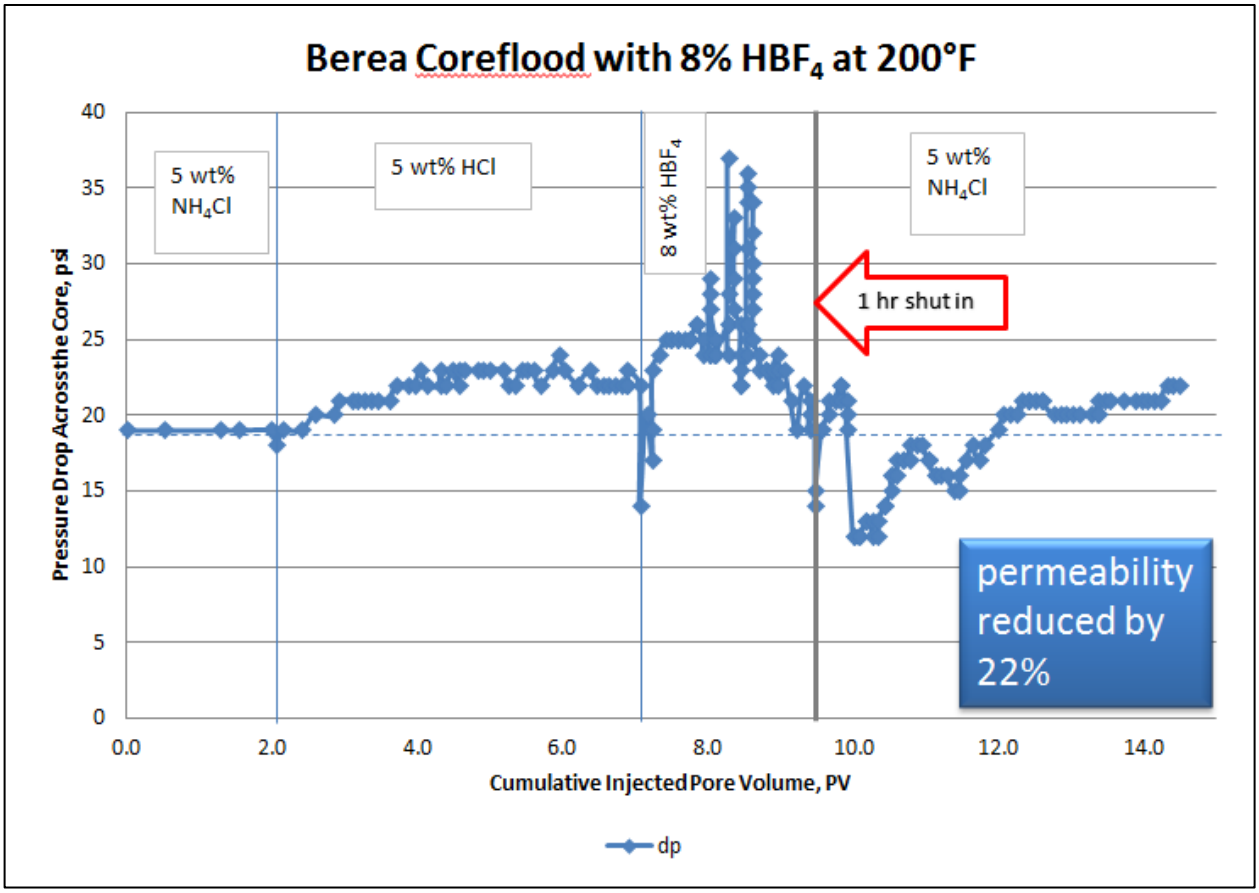

Figure 46: Pressure drop across the core during injection in Berea sandstone with 8% HBF_4 main acid at 200°F.

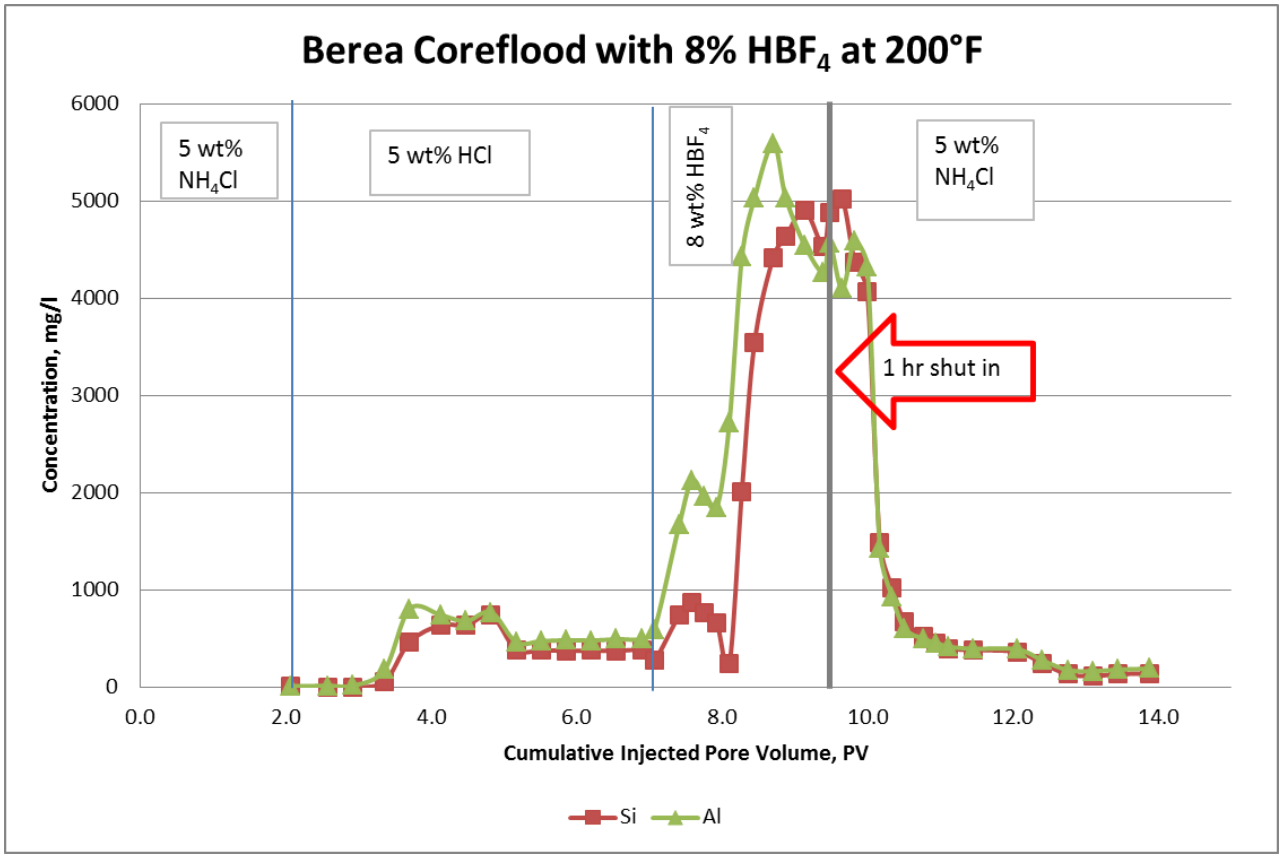

Figure 47: Si and Al concentrations in Berea coreflood effluent samples at 200°F with 8% HBF_4 main acid.

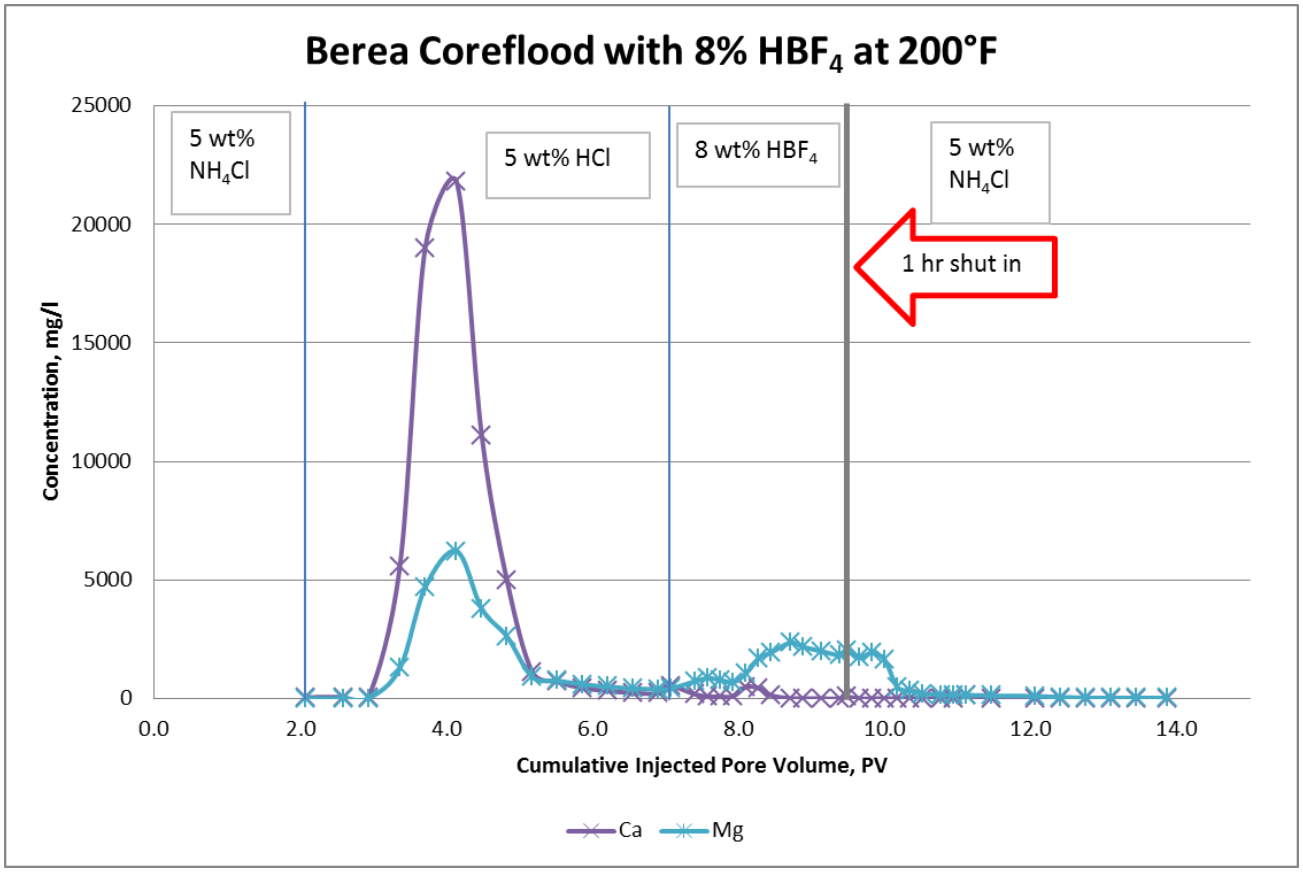

Figure 48: Ca and Mg concentrations in Berea coreflood effluent samples at 200°F with 8% HBF_4 main acid.

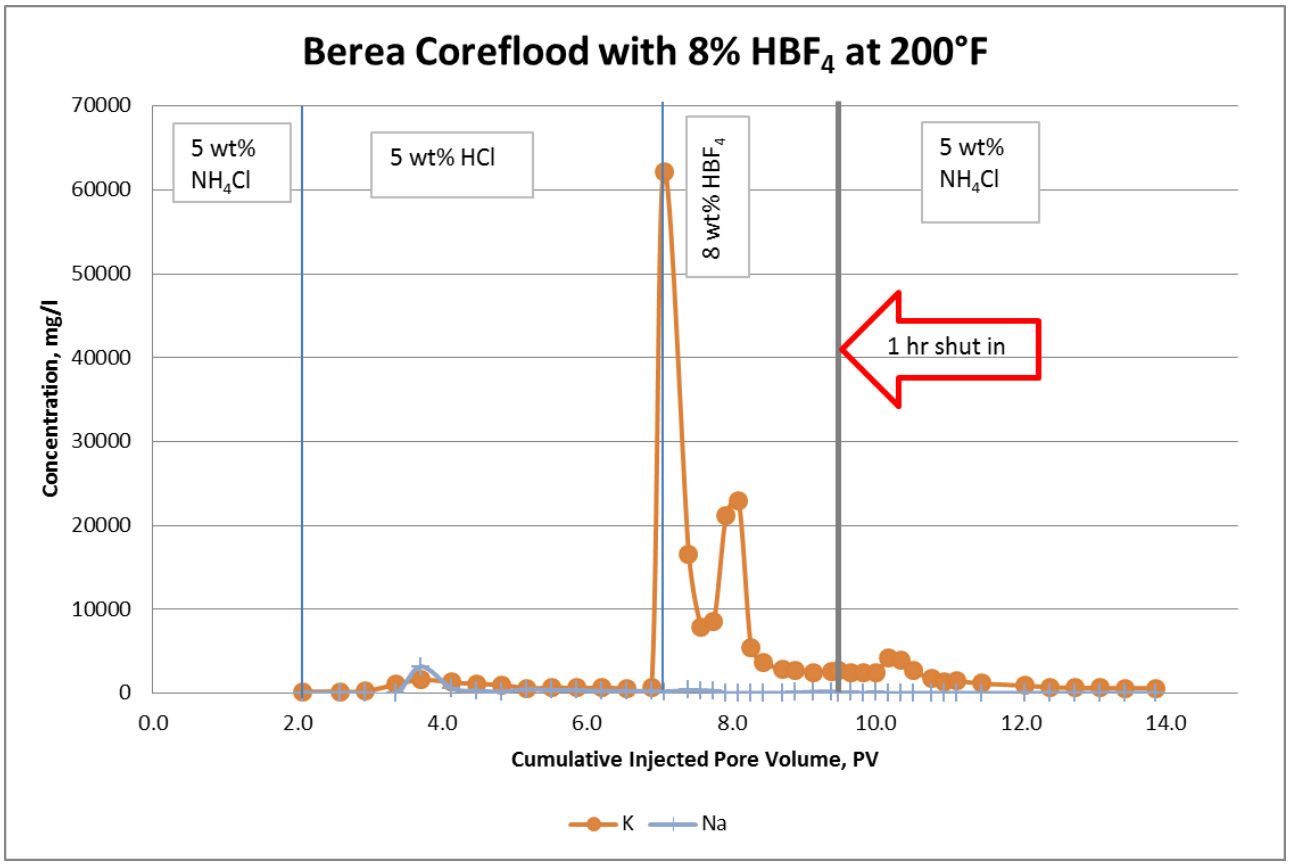

Figure 49: K and Na concentrations in Berea coreflood effluent samples at 200°F with 8% HBF_4 main acid.

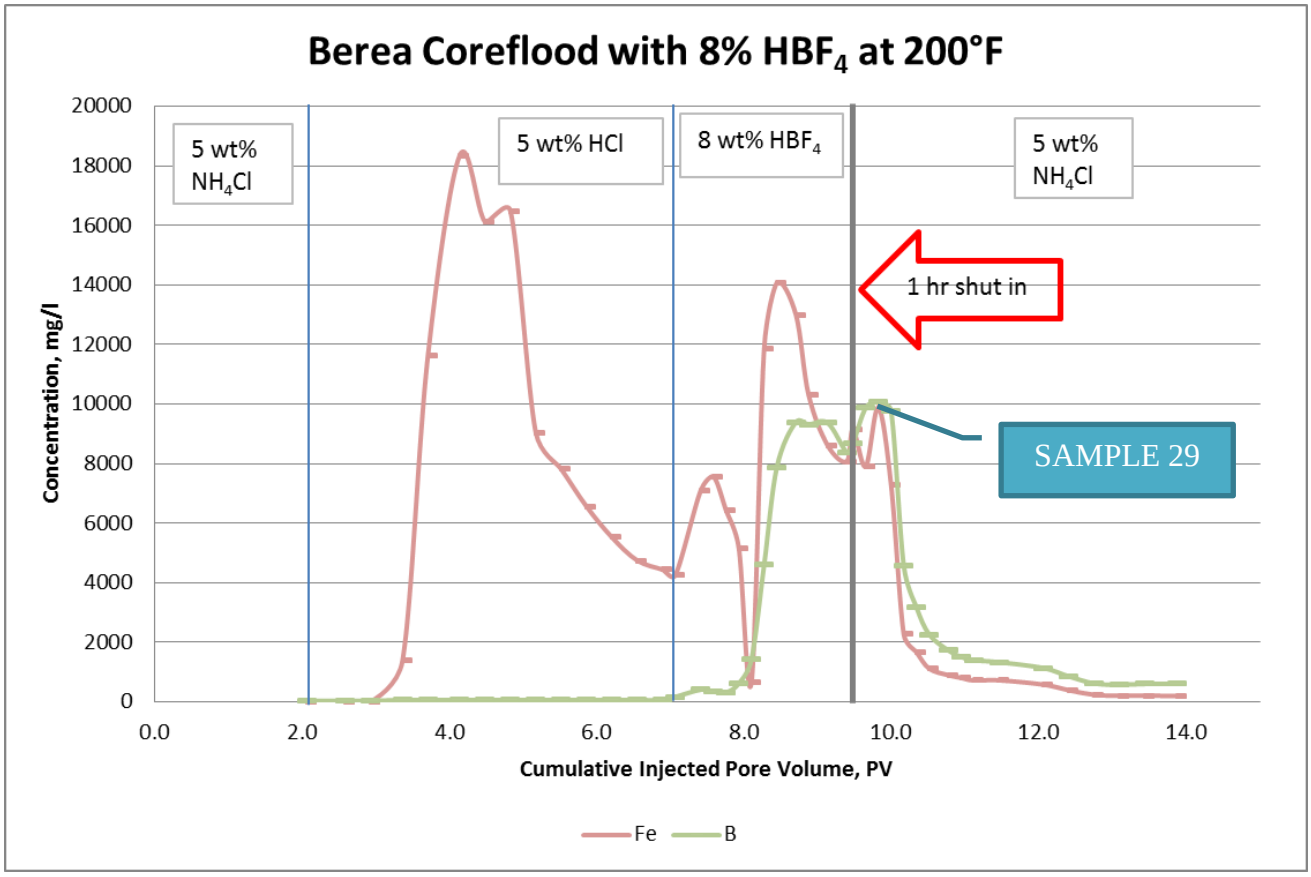

Figure 50: Fe and B concentrations in Berea coreflood effluent samples at 200°F with 8% HBF_4 main acid.

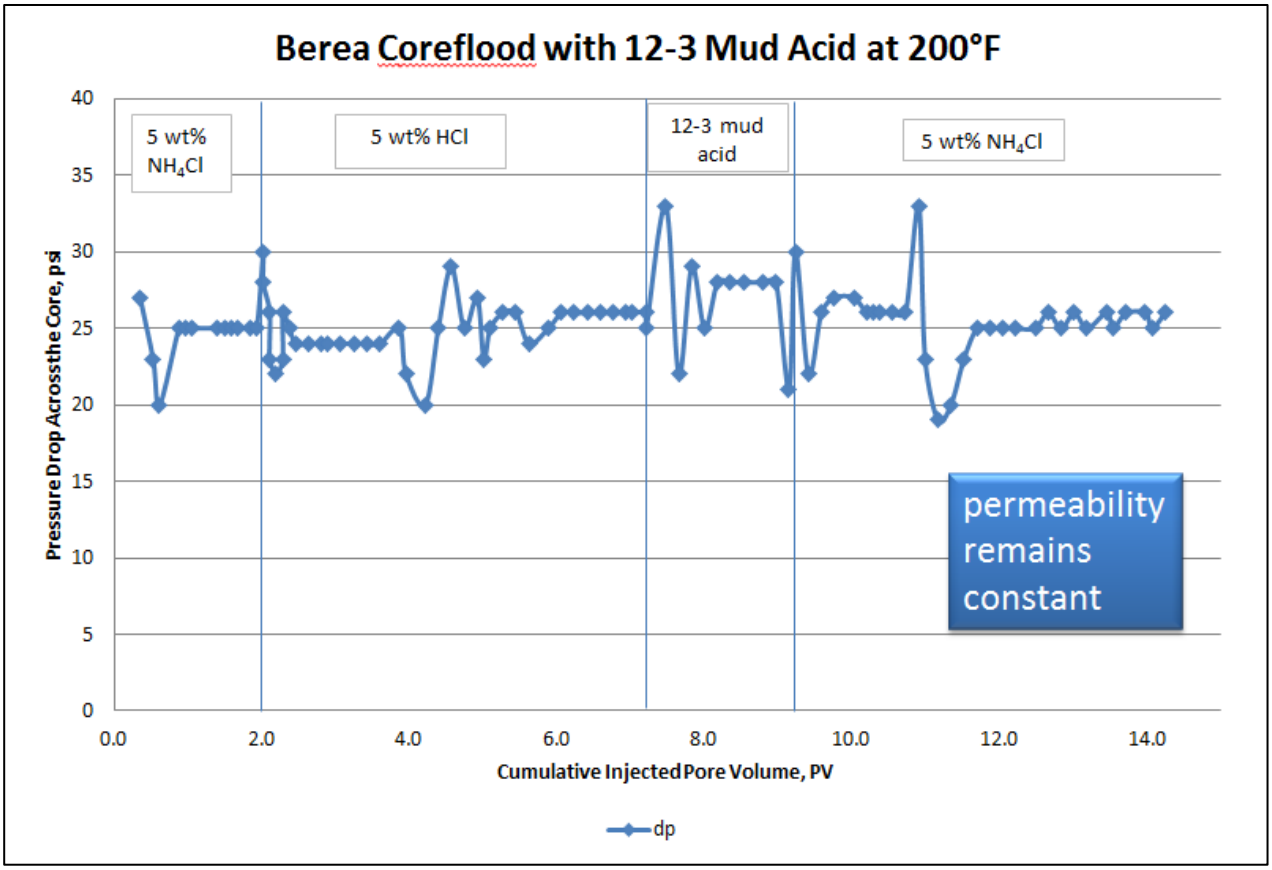

Figure 51: Pressure drop across the core during injection in Berea sandstone with 3% HBF_4 main acid at 200°F.

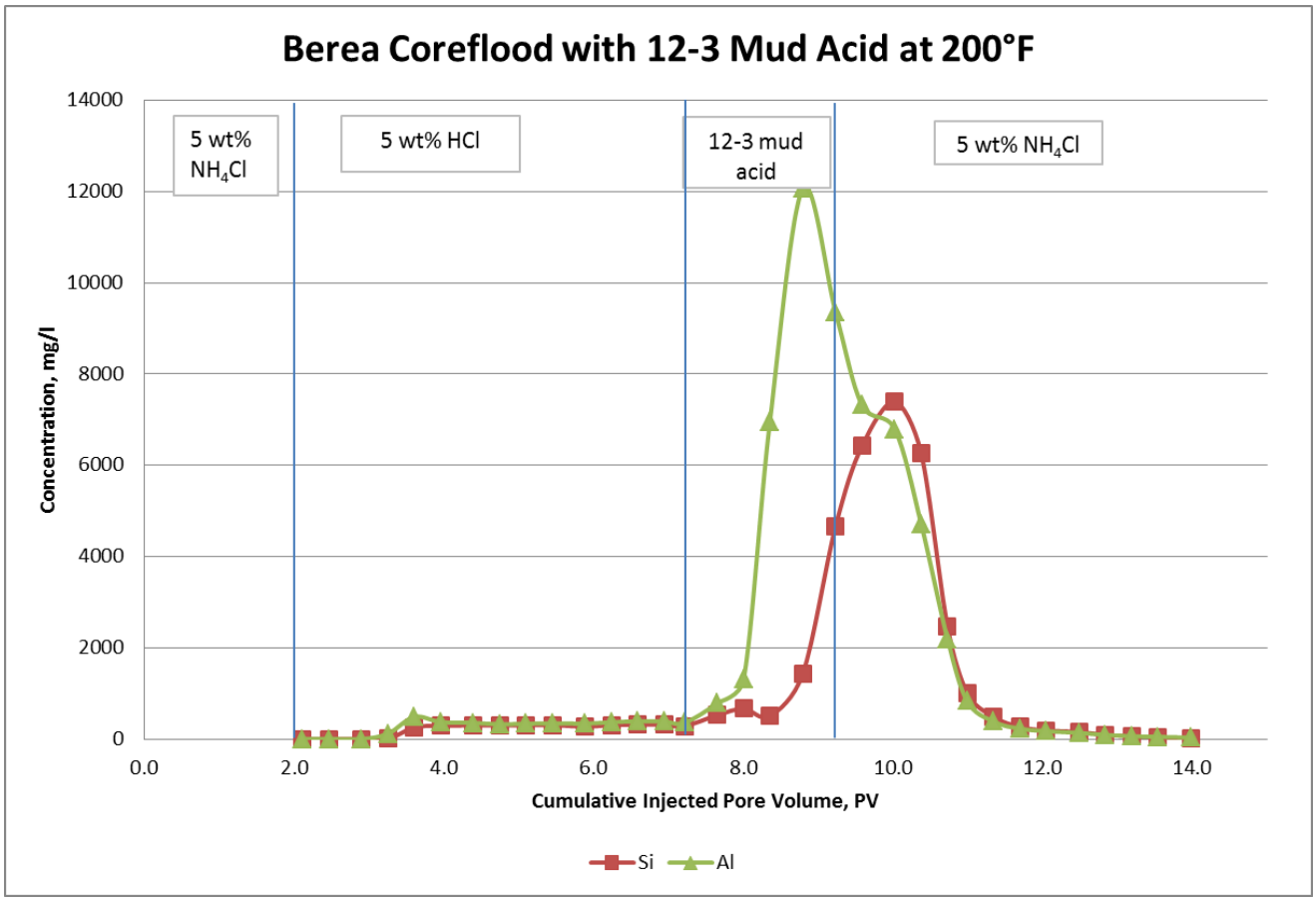

Figure 52: Si and Al concentrations in Berea coreflood effluent samples at 200°F with 12-3 mud acid as main acid.

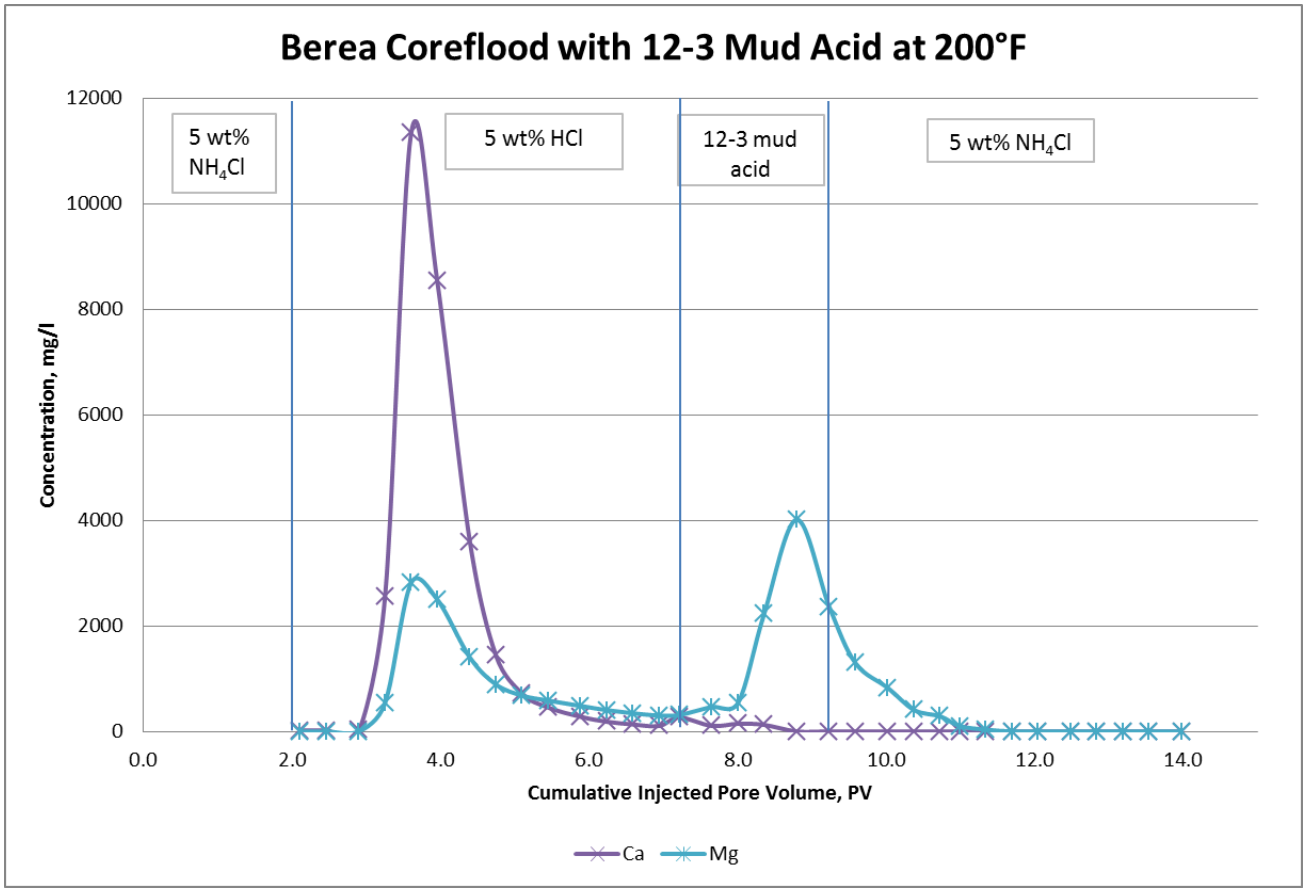

Figure 53: Ca and Mg concentrations in Berea coreflood effluent samples at 200°F with 12-3 mud acid as main acid.

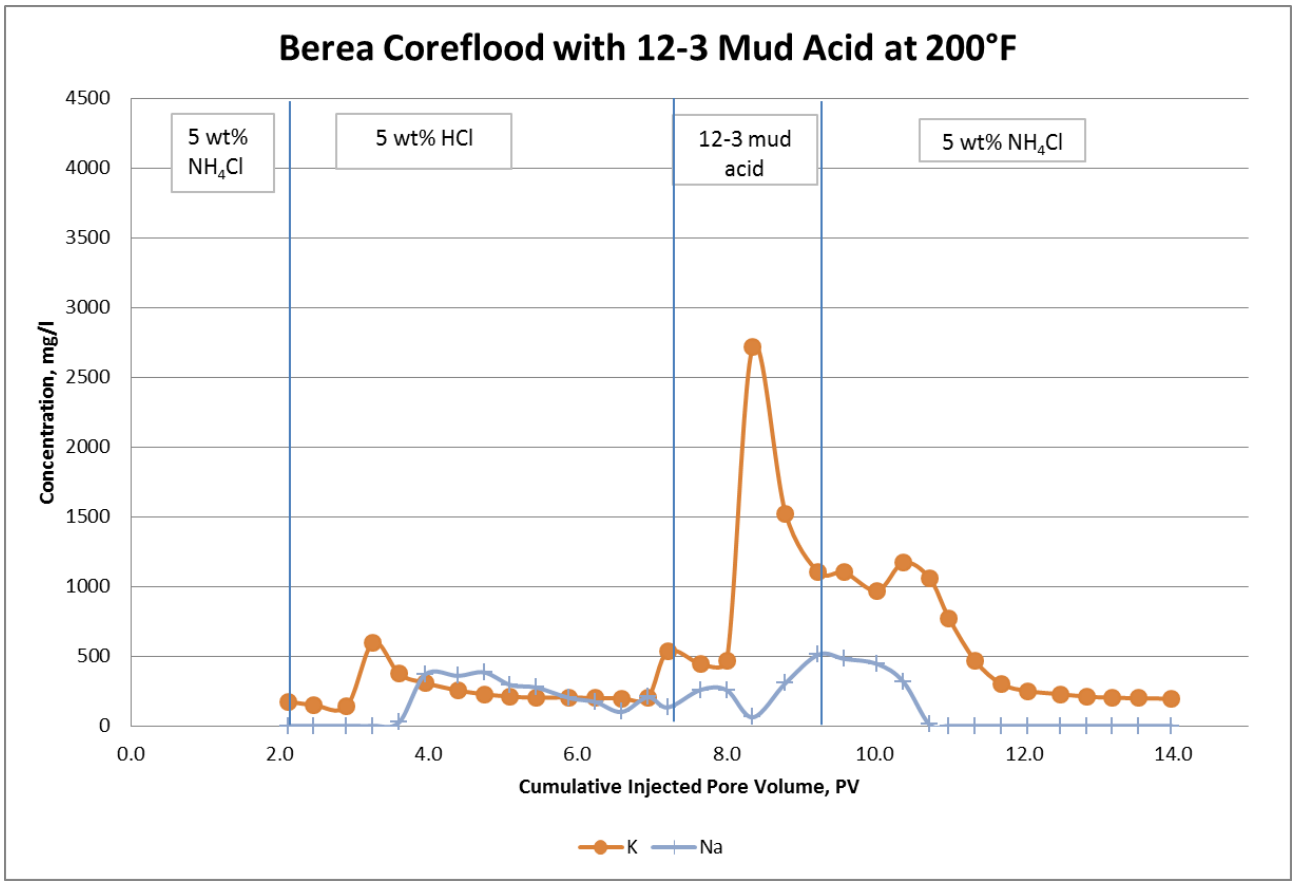

Figure 54: K and Na concentrations in Berea coreflood effluent samples at 200°F with 12-3 mud acid as main acid.

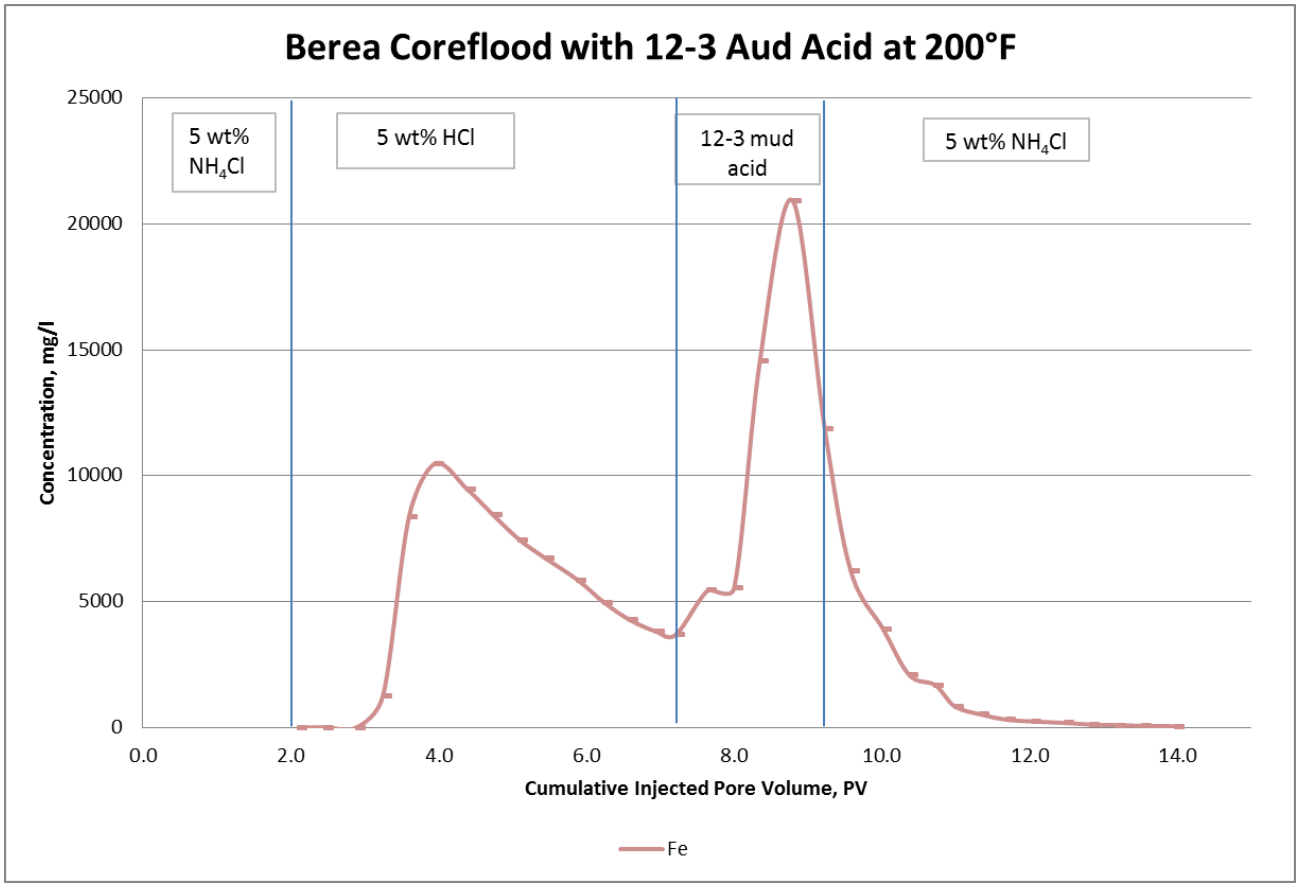

Figure 55: Fe concentration in Berea coreflood effluent samples at 200°F with 12-3 mud acid as main acid.

Both ^{11}B and ^{19}F NMR spectrum of the effluent samples from 3% HBF_4 coreflood show common species as the previous analysis of acid solutions from clay dissolution tests (Fig. 56-57), whereas the effluent samples from 8% HBF_4 coreflood gives a different spectrum. Peaks in Fig. 59 are assigned as H_3BO_3 at δ_B = 21 ppm, $BF_3(OH)^-$ at δ_B = 0 ppm, and a third minor species at δ_B = 3.5 ppm assigned as $BF_2(OH)_2^-$ to be in equilibrium with $BF_3(OH)^-$. Both species also appear in Fig. 58. Therefore, a peak at δ_F = -131 ppm is assigned as $BF_2(OH)_2^-$ and a peak at δ_F = -139 ppm is assigned as $BF_3(OH)^-$.

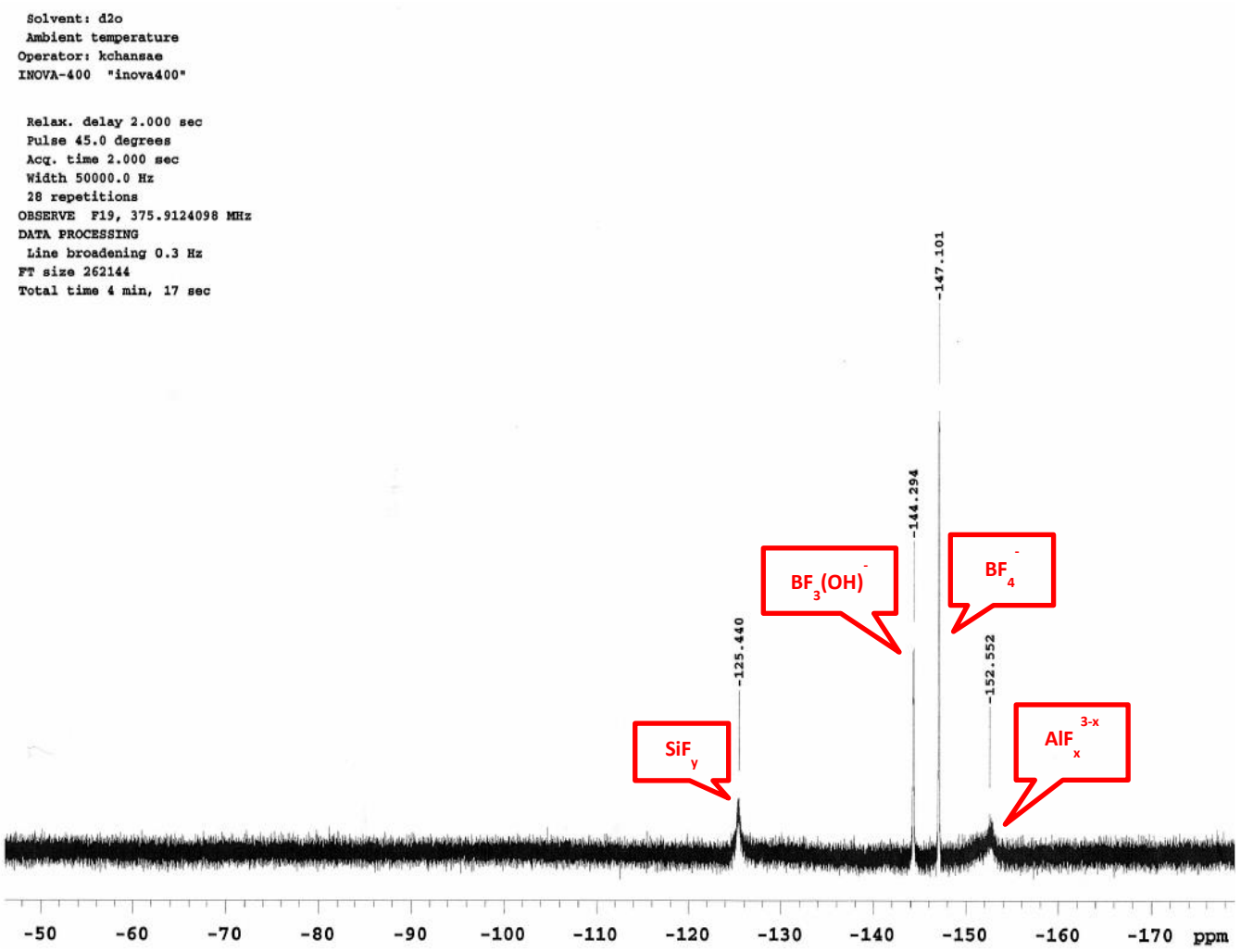

Figure 56: ^{19}F NMR spectrum of effluent sample 25 from Berea coreflood at 200°F with 3% HBF_4 main acid.

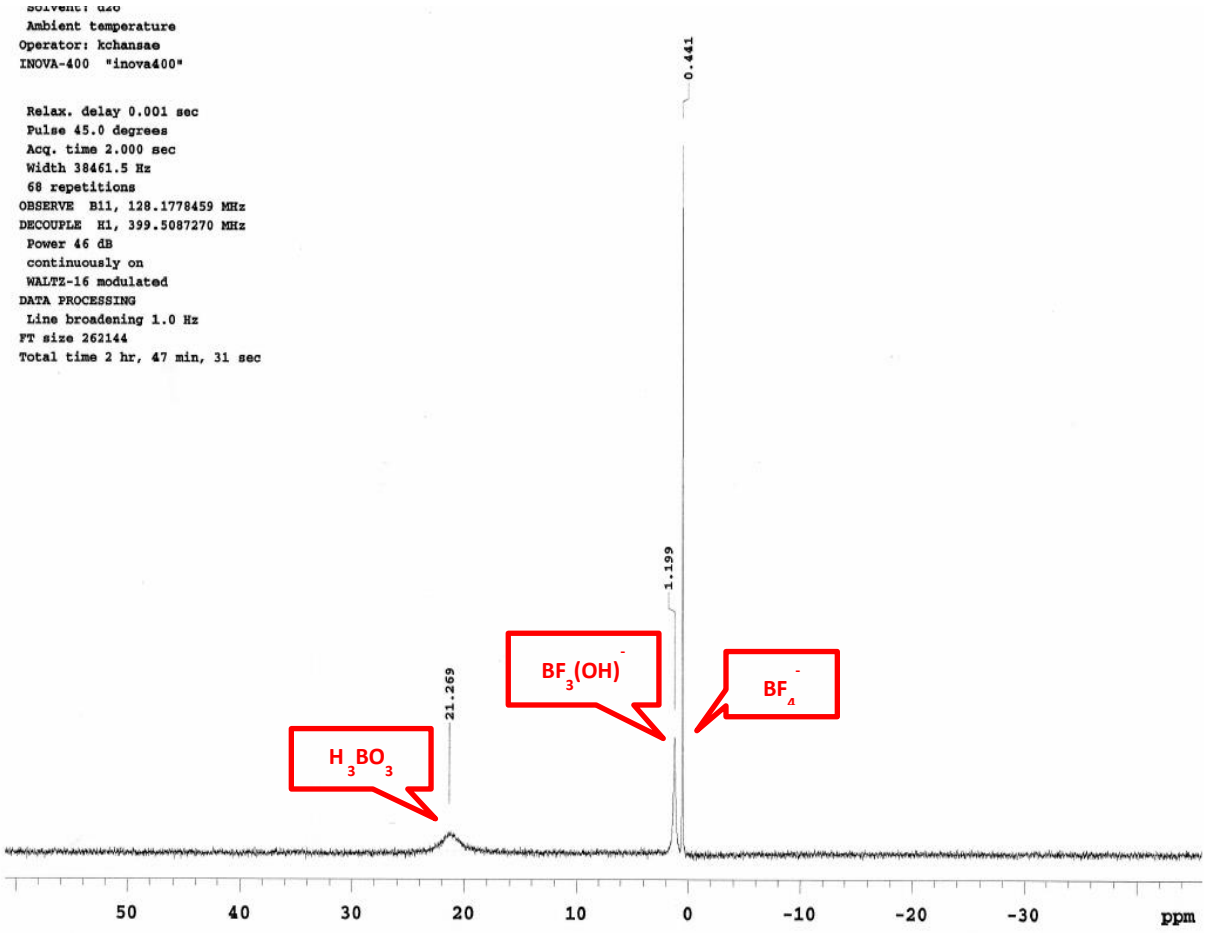

Figure 57: ^{11}B NMR spectrum of effluent sample 25 from Berea coreflood at 200°F with 3% HBF_4 main acid.

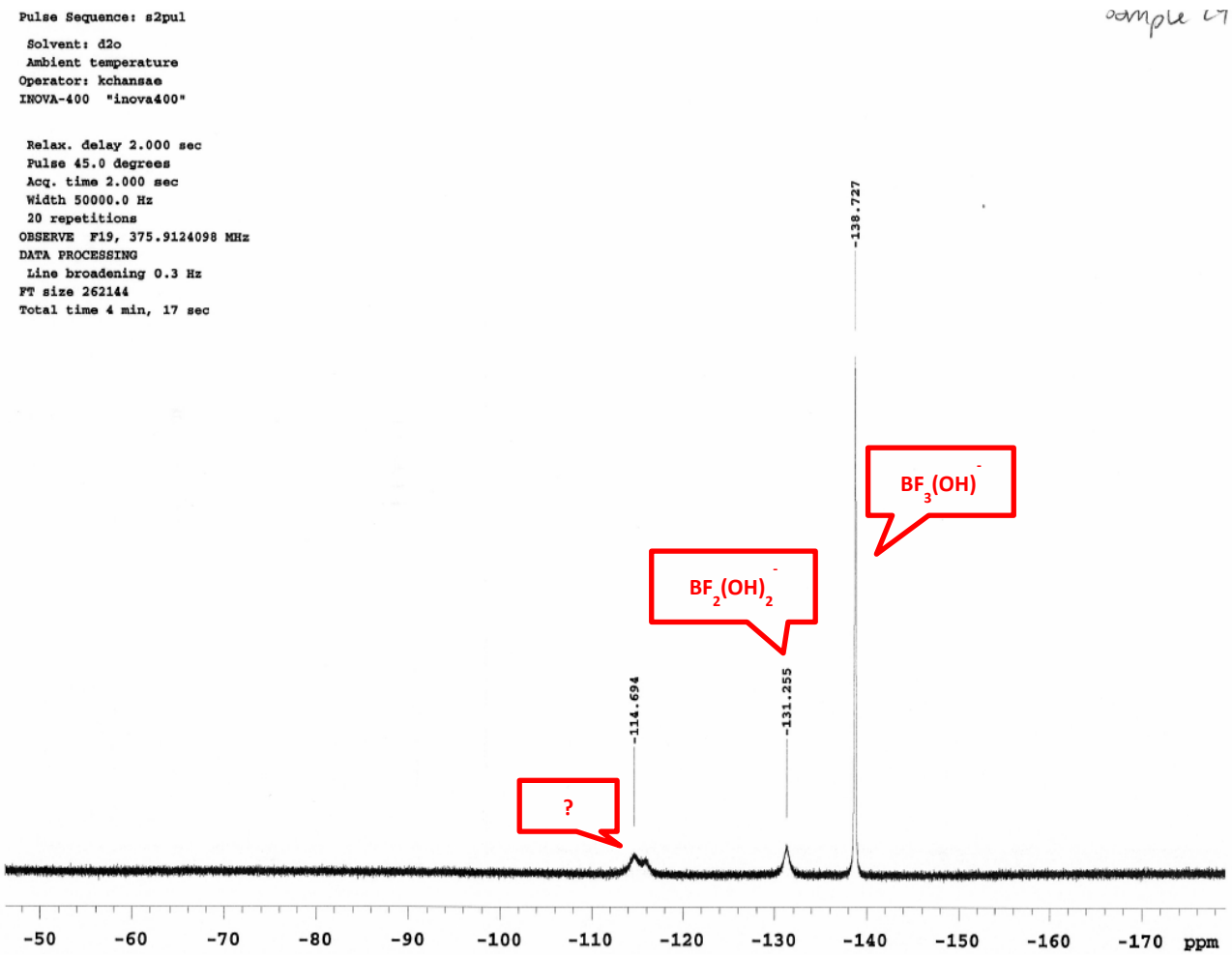

Figure 58: ^{19}F NMR spectrum of effluent sample 29 from Berea coreflood at 200°F with 8% HBF_4 main acid.

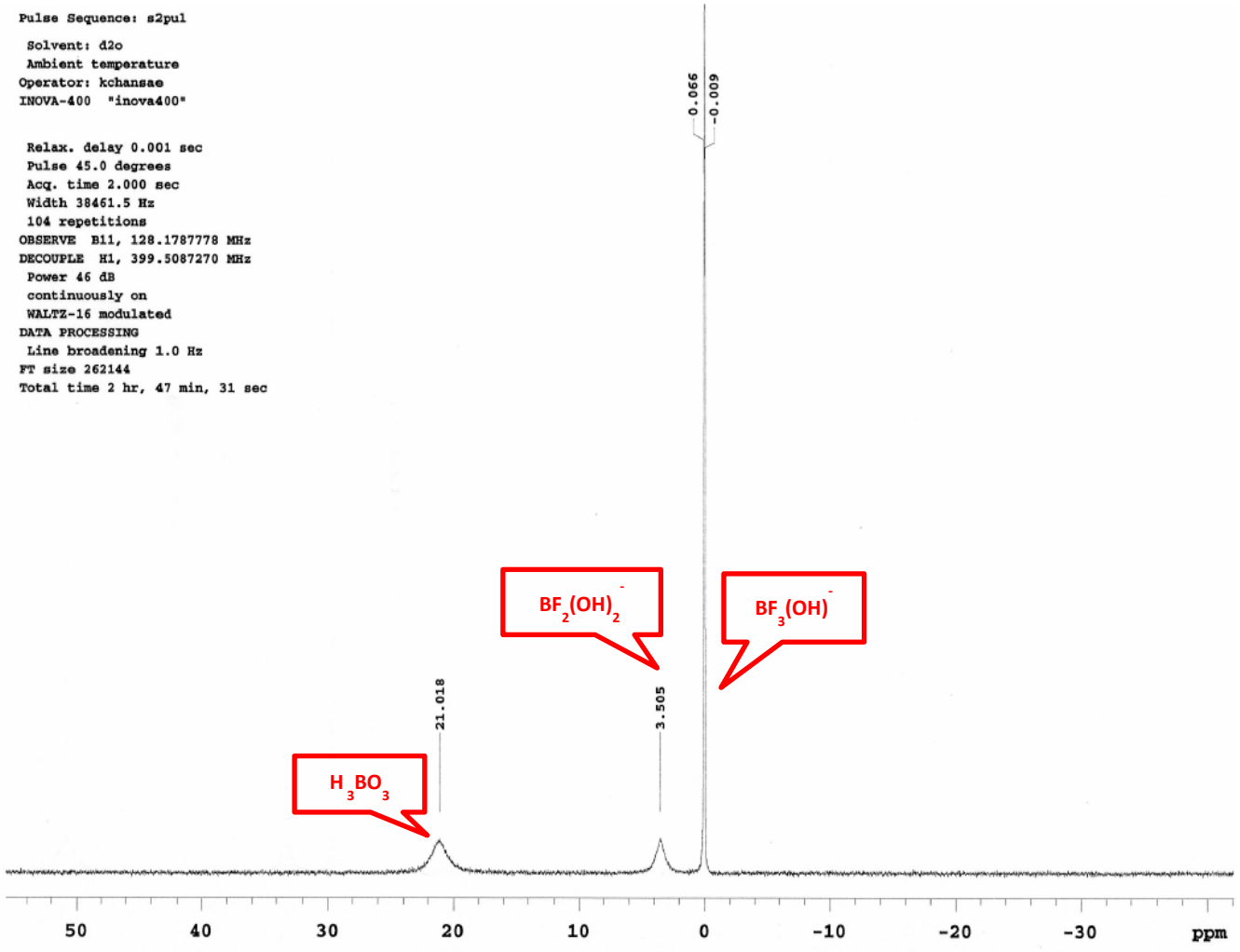

Figure 59: ^{11}B NMR spectrum of effluent sample 29 from Berea coreflood at 200°F with 8% HBF_4 main acid.

CHAPTER IV

FUTURE WORK

The borosilicate formation expected from the reaction of HBF_4 and sandstone mentioned in literature has not been investigated as of current progress. Given that this is one distinguishable benefit of HBF_4, plans have been made to accommodate it in the scope of future experimental work.

In addition, to discover the limited retardation effect of HBF_4 and to define its effective working temperature window, another set of experiments should be conducted in detail over a fine grid of temperature to pinpoint the precise temperature limit of HBF_4 for formation treatment purposes.

An effort should also be made to explain the fact why illite and bentonite responded differently to HBF_4 acid under different temperatures. With the current knowledge, this phenomenon still cannot be comprehended.

Most important of all is to continue exploring the parameters/conditions that will make HBF_4 coreflood stimulation successful in addition to understanding the relevant reactions. This would be done in comparison with mud acid and evaluated using suitable techniques to demonstrate the claimed benefits of HBF_4 over traditional mud acid.

CHAPTER V

CONCLUSIONS

It was shown in this study that the dissolution of aluminosilicates with 3% HBF_4 at 75°F will dissolve Al and Si at an equal ratio for all three clays at an effectively retarded rate and will have minor KBF_4 precipitate only in the case of illite. When reaction temperature is raised to 200°F, HBF_4 has developed a different reaction and leached all other elements from the clay structure except silica. This behavior matches the secondary reaction discussed by Gdanski.

Fresh HBF_4 hydrolytic equilibrium is established soon as it is prepared at room temperature at the given H^+ concentration. It contains three species (BF_4^-, $BF_3(OH)^-$ and HF) with BF_4^- being predominant and only a limited amount of HF.

The retardation effect of HBF_4 is evidently a strong function of temperature. Even though reaction retardation is witnessed at room temperature, it does not persist at 200°F as exhibited by the kaolinite dissolution rate of HBF_4 at 200°F, which was approximately the same as regular mud acid at this temperature. Therefore it is not recommended to apply this acid where bottomhole circulating temperature is close to or greater than 200°F.

The use of HBF_4 in formations that contains illite clay or potassium feldspar should be strictly prohibited due to the risk of KBF_4 precipitation, which can potentially cause formation damage.

Treating a six inches Berea core with 12-3 mud acid at 200°F with no shut-in did not improve the core's permeability. When using HBF_4 to treat the core at the same conditions, both 3% and 8% HBF_4 damaged the core after 1 hour of shut-in. This damage is probably due to silica precipitation, as it is a known product of the secondary reaction which goes to completion at this temperature. The different responses of core's final permeability after mud acid and HBF_4 is believed to be induced by silica-precipitate-blocked pore throats developed over the period of HF being shut-in in the case of HBF_4.

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APPENDIX A

A-1. Fluoboric Acid Material Safety Data Sheet

Material Safety Data Sheet
Fluoboric acid MSDS

Wednesday, March 5, 2014 at 8:45pm

Product and Company Identification

Product Name: Fluoboric acid

Catalog Codes: SLF1771

CAS#: 16872-11-0

RTECS: ED2685000

TSCA: TSCA 8(b) inventory: Fluoboric acid

CI#: Not available.

Synonym: Tetrafluoroboric acid

Chemical Formula: HBF4

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call: 1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Fluoboric acid	16872-11-0	100

Toxicological Data on Ingredients: Fluoboric acid LD50: Not available. LC50: Not available.

Section 3: Hazards Identification

Potential Acute Health Effects:
Extremely hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Corrosive to skin and eyes on contact. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

Potential Chronic Health Effects:
Extremely hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance is toxic to lungs, mucous membranes. Repeated or prolonged exposure to the substance can produce target organs damage. Repeated or prolonged contact with spray mist may produce chronic eye irritation and severe skin irritation. Repeated or prolonged exposure to spray mist may produce respiratory tract irritation leading to frequent attacks of bronchial infection. Repeated or prolonged inhalation of vapors may lead to chronic respiratory irritation.

Section 4: First Aid Measures

Eye Contact:
Check for and remove any contact lenses. Immediately flush eyes with running water for at least 15 minutes, keeping eyelids open. Cold water may be used. Do not use an eye ointment. Seek medical attention.

Skin Contact:
If the chemical got onto the clothed portion of the body, remove the contaminated clothes as quickly as possible, protecting your own hands and body. Place the victim under a deluge shower. If the chemical got on the victim's exposed skin, such as the hands : Gently and thoroughly wash the contaminated skin with running water and non-abrasive soap. Be particularly careful to clean folds, crevices, creases and groin. Cold water may be used. If irritation persists, seek medical attention. Wash contaminated clothing before reusing.

Serious Skin Contact:
Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek medical attention.

Inhalation: Allow the victim to rest in a well ventilated area. Seek immediate medical attention.

Serious Inhalation:
Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. WARNING: It may be hazardous to the person providing aid to give mouth-to-mouth resuscitation when the inhaled material is toxic, infectious or corrosive. Seek immediate medical attention.

Ingestion:
Do not induce vomiting. Loosen tight clothing such as a collar, tie, belt or waistband. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek immediate medical attention.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: Non-flammable.

Auto-Ignition Temperature: Not applicable.

Flash Points: Not applicable.

Flammable Limits: Not applicable.

Products of Combustion: Not available.

Fire Hazards in Presence of Various Substances: Not applicable.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available.

Fire Fighting Media and Instructions: Not applicable.

Special Remarks on Fire Hazards: Not available.

Special Remarks on Explosion Hazards: Not available.

Section 6: Accidental Release Measures

Small Spill:
Dilute with water and mop up, or absorb with an inert dry material and place in an appropriate waste disposal container.

Large Spill:
Corrosive liquid. Stop leak if without risk. Absorb with DRY earth, sand or other non-combustible material. Do not get water inside container. Do not touch spilled material. Use water spray curtain to divert vapor drift. Prevent entry into sewers, basements or confined areas; dike if needed. Call for assistance on disposal.

Section 7: Handling and Storage

Precautions:
Keep container dry. Do not breathe gas/fumes/ vapour/spray. Never add water to this product In case of insufficient ventilation, wear suitable respiratory equipment If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes Keep away from incompatibles such as metals, alkalis. May corrode glass. Store in an appropriate container.

Storage:
May corrode metallic surfaces. Store in a metallic or coated fiberboard drum using a strong polyethylene inner package. May corrode glass. Store in an appropriate container. Corrosive materials should be stored in a separate safety storage cabinet or room.

Section 8: Exposure Controls/Personal Protection

Engineering Controls:
Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapors below their respective threshold limit value.

Personal Protection:
Face shield. Full suit. Vapor respirator. Be sure to use an approved/certified respirator or equivalent. Gloves. Boots.

Personal Protection in Case of a Large Spill:
Splash goggles. Full suit. Vapor respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits: Not available.

Section 9: Physical and Chemical Properties

Physical state and appearance: Liquid.

Odor: Odorless.

Taste: Not available.

Molecular Weight: 87.81 g/mole

Color: Colorless.

pH (1% soln/water): Not available.

Boiling Point: Decomposes. (130°C or 266°F)

Melting Point: Not available.

Critical Temperature: Not available.

Specific Gravity: 1.84 (Water = 1)

Vapor Pressure: Not available.

Vapor Density: Not available.

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: Not available.

Ionicity (in Water): Not available.

Dispersion Properties: See solubility in water, methanol.

Solubility:
Easily soluble in cold water. Soluble in methanol.

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Not available.

Incompatibility with various substances: Extremely reactive or incompatible with metals, alkalis.

Corrosivity:
Extremely corrosive in presence of steel, of aluminum, of zinc, of copper. Highly corrosive in presence of glass, of stainless steel(304), of stainless steel(316).

Special Remarks on Reactivity: Decomposes on heating.

Special Remarks on Corrosivity: Not available.

Polymerization: No.

Section 11: Toxicological Information

Routes of Entry: Eye contact. Inhalation. Ingestion.

Toxicity to Animals:
LD50: Not available. LC50: Not available.

Chronic Effects on Humans: The substance is toxic to lungs, mucous membranes.

Other Toxic Effects on Humans: Extremely hazardous in case of skin contact (irritant), of ingestion, of inhalation.

Special Remarks on Toxicity to Animals: Not available.

Special Remarks on Chronic Effects on Humans: Not available.

Special Remarks on other Toxic Effects on Humans: Not available.

Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not available.

Products of Biodegradation:
Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The products of degradation are more toxic.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:

Section 14: Transport Information

DOT Classification: CLASS 8: Corrosive liquid.

Identification: : Fluoroboric acid : UN1775 PG: II

Special Provisions for Transport: Not available.

Section 15: Other Regulatory Information

Federal and State Regulations: TSCA 8(b) inventory: Fluoboric acid

Other Regulations: OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200).

Other Classifications:

WHMIS (Canada):
CLASS D-2A: Material causing other toxic effects (VERY TOXIC). CLASS E: Corrosive liquid.

DSCL (EEC):
R38- Irritating to skin. R41- Risk of serious damage to eyes.

HMIS (U.S.A.):

Health Hazard: 3

Fire Hazard: 0

Reactivity: 0

Personal Protection:

National Fire Protection Association (U.S.A.):

Health: 3

Flammability: 0

Reactivity: 0

Specific hazard:

Protective Equipment:
Gloves. Full suit. Vapor respirator. Be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate. Face shield.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

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A-2. HBF_4 unit cost

Per 1 kilogram of 3% HBF_4:

	(g)	Unit cost	Cost
H_2O	786.75	$ 0.01	$ 7.87
NH_4HF_2	42.75	$ 0.07	$ 2.96
H_3BO_3	23.17	$ 0.07	$ 1.67
HCl	147.33	$ 0.01	$ 2.18
Total	**1000.00**		**$ 14.67**